DOCTOR OF PHILOSOPHY

To Enable the Processing of New Complex High Performance Alloys by Improving the Capacity and Performance of Continuous Casting Equipment

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To Enable the Processing of New Complex High Performance Alloys by Improving the Capacity and Performance of Continuous Casting Equipment

By

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University of Dundee
for the degree of Doctor of Philosophy (PhD)

Table of Content

List of Figures

List of Tables

List of Acronyms

ASTM - American Society for Testing and Materials

CDA - Copper Development Association

DHP Copper - Deoxidized High Phosphorus Copper

EC - Electrical Conductivity

ECAP - Equal Channel Angular Pressing

EDX - Energy Dispersive X-ray

ICP-OES - Inductively coupled plasma - Otical Emission Spectroscopy

LME grade a copper - London Metal Exchange grade a copper

MIG - Metal Inert Gas

MPa - MegaPascal

MS - Mass spectrometry

OFC - Oxygen Free Copper

OD - Outside Diameter

OM - Optical Microscopy

PLC - Programmable Logic Controller

PPE - Personal Protective Equipment

R&D - Research and Development

SDAS - Secondary Dendrite Arm Spacing

SEM - Scanning Electron Microscope

Spark - OES - Spark Optical Emission Spectroscopy

TIG - Tungsten Arc Welding

UTS - Ultimate Tensile Strength

XRD - X-Ray Diffraction

XRF - X-Ray Fluorescence

Declaration

I, "Ehsaan-Reza Bagherian" declare that the thesis entitled:

To enable the Processing of New Complex High Performance Alloys by Improving the Capacity and Performance of Continuous Casting Equipment

and the work presented in it are my own and has been generated by me as the result of my own original research.

I confirm that:

1. This work was done wholly or mainly while in candidature for a research degree at this University;
2. Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated;
3. Where I have consulted the published work of others, this is always clearly attributed;
4. Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work;
5. I have acknowledged all main sources of help;
6. Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself;
7. Parts of this work have been published (in the list of publications).
8. I also declare that if has not been previously or concurrently submitted for any other degree at University of Dundee or other institutions.

Ehsaan-Reza Bagherian

Date of Submission

Certification

I, “Professor A. Abdolvand” of the School of Science & Engineering, hereby certify that Ehsaan-Reza Bagherian has spent the required number of terms at reseach under my supervision and that he has fulfilled the condition of the Ordinance of the University of Dundee so that he is qualified to submit the following thesis for the degree of Doctor of Philosophy.

Amin Abdolvand

List of Publications

The following publications of the author are related to this thesis:

1- Ehsaan-Reza Bagherian, Yongchang Fan, Mervyn Cooper , Brian Frame, Amin Abdolvand: *Investigation of the Distribution of Lead in three Different Combinations of Brass Feedstock*. **INTERNATIONAL JOURNAL OF METALCASTING**, Volume: **10**, Pages: **322-328** (**2016**).

2- Ehsaan-Reza Bagherian, Yongchang Fan, Mervyn Cooper, Brian Frame and Amin Abdolvand: *Effect of water flow rate, casting speed, alloying elements and pull distance on tensile strength, elongation percentage and microstructure of continuous cast copper alloys*. **METALLURGICAL RESEARCH & TECHNOLOGY**, Volume: **113**, Pages: **308-321** (**2016**).

3- Ehsaan-Reza Bagherian, Yongchang Fan, Mervyn Cooper, Brian Frame and Amin Abdolvand: *Effect of Melt Temperature, Cleanout Cycle, Continuous Casting Direction (Horizontal / Vertical) and Super-Cooler Size on Tensile Strength, Elongation Percentage and Microstructure of Continuous Cast Copper Alloy*. **METALLURGICAL RESEARCH & TECHNOLOGY**, Volume: **113**, Pages: **502-518** (**2016**).

4- Ehsaan-Reza Bagherian, Colin Bell, Mervyn Cooper, Yongchang Fan, Brian Frame and Mervyn Rose, *Analysis and Quantification of Grain Size of Various DHP Copper Tubes Manufacturing Processes*. **JOURNAL OF ADVANCED MATERIALS RESEARCH,** Published online: 06 December 2013, Vol. 856 (2014) pp 241-245.

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Related conference presentation of the author:

5- BAGHERIAN Ehsaan-Rez, FAN Yongchang, COOPER Mervyn, FRAME Brian and ABDOLVAND Amin, *EFFECT OF ANTIMONY ADDITION RELATIVE TO MICROSTRUCTURE AND MECHANICAL PROPERTIES OF CONTINUOUS CAST LEAD ALLOY*, **25th International Conference on Metallurgy and Materials**, Brno, Czech Republic, May 25th - 27th 2016.

6- BAGHERIAN Ehsaan-Rez, FAN Yongchang, COOPER Mervyn, FRAME Brian and ABDOLVAND Amin, *ANALYSIS AND QUANTIFICATION OF MECHANICAL PROPERTIES OF VARIOUS DHP COPPER TUBES MANUFACTURING PROCESSES USING DRIFT EXPANDING TEST*, **25th International Conference on Metallurgy and Materials**, Brno, Czech Republic, May 25th - 27th 2016.

7- Ehsaan-Reza Bagherian, Yongchang Fan, Mervyn Cooper, Brian Frame and Amin Abdolvand: *Analysis and Quantification of Continuous Casting of Copper Alloys*, Poster presentation at **SUPA 2016 Annual Gathering** University of Strathclyde, Technology & Innovation Centre, Glasgow, May 2016.

8- Ehsaan-Reza BAGHERIAN, Colin BELL, Mervyn COOPER, Yongchang FAN, Brian FRAME and Amin ABDOLVAND, *Influence of Casting Speed on The Structure and Mechanical Properties of Continuous Cast DHP Copper Tube*, **23rd International Conference on Metallurgy and Materials**, Brno, Czech Republic, May 21st – 23rd 2014.

Other publication of the author which not related to this work:

9- Ehsaan-Reza.Bagherian, Mohd Khairol Ariffin and Shamsuddin Sulaiman, *DEVELOPMENT OF A CERAMIC FOAM FILTER FOR FILTERING MOLTEN ALUMINUM ALLOY IN CASTING PROCESSES,* **International Journal of Research in Engineering and Technology**: Published online: March 2015, Volume: 04 Issue: 03.

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11- Ehsaan-Reza.Bagherian, Mohd Khairol Ariffin and Shamsuddin Sulaiman, *POSITIONING CERAMIC FOAM FILTERS IN GATING SYSTEM FOR CASTING ALLOY FILTRATION*. **4th International Conference on Recent Advances in Materials, Minerals and Environment and 2nd Asian Symposium on Minerals and Processing (RAMM & ASMP 2009)**, Issue Date: 1-Jun-2009. Publisher: Universiti Sains Malaysia (USM), 11800 USM Penang, Malaysia.

12- Ehsaan-Reza.Bagherian, Mohd Khairol Ariffin and Shamsuddin Sulaiman, *Casting Alloy Filtration with Ceramic Foam Filter*. **International Conference on Advances in Mechanical Engineering 2009-ICAME 2009.** 24th to 25th June 2009. KUALA LUMPUR, Malaysia

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Abstract

In a high competitive market, the development of new alloys, new applications, price pressure and increases in product forces quality wire manufacturers to ask for increased mechanical characteristics without losing conductivity. As a particular example, development of new copper alloys such as CuZr, CuSn, CuMg and CuAg have been developed for automotive cables.

Continuous extrusion is currently the most prevalent manufacturing technology in terms of chemical composition, mechanical properties and electrical properties, resulting in the production of high quality rods. However, continuous casting has good potential to also be adapted to the mass production of various copper alloy wires.

Comparison of the continuous casting process to other thermal methods such as continuous extrusion highlighted that, in general, the mechanical properties of continuous cast materials are lower than that of material from thermomechanical methods. However, continuously cast alloys rods are cheap to produce and simple to manufacture.

So, the key aims of this research were (a) to increase the understanding of the solidification behaviour of some industrially important continuously cast non-ferrous alloys, (b) to define an increased range of alloys and downstream processing techniques which could be performed using continuous casting technology, (c) to determine improved continuous casting process validation capabilities and (d) to define new capabilities in terms of casting equipment.

The majority of this PhD thesis was focused on improving the current continuous casting technologies and development of casting capability of a range of copper and non-copper alloys.

The analysis in this PhD thesis illustrated that the metallurgical and mechanical properties of components mainly produced by continuous casting are acceptable, and that this method could be a replacement production method for materials such as lead alloys and various copper alloy rod, e.g. CuMg and CuAg.. However, in the case of Deoxidized High Phosphorus (DHP) copper tubes, the performance of the as-cast material was significantly lower than that of from extrusion or planetary rolling process.

This PhD thesis also makes comment on the parameters controlling the solidification process in order to improve the quality of as cast alloys rods/tubes. Using specific casting parameters, a significant difference based on tensile strength and elongation percentage has been illustrated, and it was found that these parameters could improve the mechanical properties of continuously cast copper rods and tubes. This significant difference is as a result only of the change in casting parameters, with no difference in the chemical composition of the material, or the general method of production. These parameters were (1) water flow rate, (2) casting speed, (3) pull distance, (4) melt temperature, (5) cleanout cycle, (6) continuous casting direction and (7) super-cooler size.

The new knowledge created and understanding gained during the course of this research improved the company's capability in the marketplace, enabling it to supply equipment with improved competitive capabilities and the potential to enter new markets, leading to sales growth in existing sectors and significant longer-term growth into new technically challenging application areas.

Chapter 1 - Introduction

1.1 Background of the Study

Copper and copper alloys are ranked third behind iron and steel materials as well as aluminium alloys in industry. Copper is one of the oldest known metals, which can be used in various ranges of applications such as electronic devices, electrical wiring, cables, refrigeration tubing and plumbing, due to beneficial characteristics such as excellent heat conductivity and electrical conductivity, good corrosion resistance and good machinability.

Globally, one million tons of copper metals each year are produced by the continuous casting process. Continuously cast products are comparatively cheaper than those produced by extrusion processes. Considering the advantages of continuously cast products, including lower costs, if their metallurgical and mechanical properties are acceptable, this method can replace other manufacturing processes. Therefore, understanding the process and its parameters is very useful and essential.

1.2 Problem Statement

Rautomead Limited specialise in the design, manufacture and sale of continuous casting equipment for non-ferrous metals/alloys (mainly copper and copper alloys), and precious metals (gold, silver and silver alloys). There are now more than 400 Rautomead total machines (for producing wire/cable feedstock or minting coins/jewellery sheet) in operation in over 47 different countries around the world.

The company is the global market leader in small/medium size (less than 10k tonnes p.a.) machines with its customers mainly working in wire production.

To support machine sales, Rautomead undertakes R&D in metals formation and processing technologies development, with specific emphasis on lighter weight and higher conductivity alloys.

Rautomead growth markets (customers producing wire/cable/parts for the automotive, aerospace and high speed rail) are technology driven, requiring new alloys which can be processed to produce thinner, lighter and higher conductivity wire/foil/parts. To address these opportunities, the business aims to understand how its machines, and their processing capabilities, can be modified to produce complex alloy castings/feedstocks. The company's extensive experience in continuous casting indicates that its knowledge is considerable. However, as the potential applications become more demanding in terms of the alloys and the cast product's characteristics, there is a need to understand why certain parameters impact the downstream processing performance of its casting machine production and to investigate improvement mechanisms.

The continuous drive by end-users for higher performance materials means that growth opportunities will involve providing a capability to efficiently cast sophisticated alloys to a high quality standard enabling reliable downstream processing and higher value final products. These machines also generate higher margins (profit) than standard casting machines. Improving the understanding of the design and process variables is necessary to effectively exploit these high margin opportunities.

Competition from low wage-rate countries (such as China or India), although not present in a serious way at the moment, is a possibility. By developing its intellectual assets in casting process knowledge, Rautomead can maintain its lead over competitors. However, the company lacks the knowledge and expertise to undertake multi-scale investigations of fundamental material behaviour and the skills to analyse material data with the aim of creating reliable models to inform product design based on knowledge of different materials properties.

1.3 Objectives

The objective of present research is to understand the fundamental material behaviour when applied to Rautomead's continuous casting processes, with the aim of creating reliable models of good practice. The anticipated outcomes would lead to:

- Comparison of continuous casting and the other additive manufacturing processes such as extrusion, drawing and planetary rolling.
- The development of casting capability of a range of copper alloys using various alloying elements such as Zr, Mg, Sn, Ag.
- The development of casting capability for non-copper metals and alloys such as lead alloys by continuous casting technology.
- The development of casting capability to produce DHP copper tube
- The development of casting capability to produce new brass.

This would ultimately enhance the company's competitiveness and open up new markets. These can also inform and improve the product and process design for current products and for continuous cast non-ferrous alloy products, especially copper and copper alloys.

1.4 Thesis Layout

This thesis is structured into nine chapters, and starts with an introduction and literature review to clarify the advantages and limitations of the continuous casting process and improving methods. It will include a detailed elaboration of the theory and mechanism of grain refinement techniques, the benefit of thermal methods, and the limitations of chemical and mechanical methods. Furthermore, this thesis will present methodology comprising (a) differences between continuous casting and other thermal mechanical methods and (b) efficiency of various casting parameters in mechanical properties of continuously cast product in order to understand the effect of grain refinement techniques using the thermal method. Results of experiments and data analysis overall will be discussed and explained in individual chapters. The final conclusions of this study are explained in each chapter.

This PhD project is focused on continuous casting of copper and copper alloy produced by Rautomead casting machinery. In particular, significant progress has been made in establishing a range of relevant analysis techniques, and a significant amount of data has been provided that has directly benefited a number of research and development projects. Research work has been mainly focused on the material characterisation of mostly copper alloy rods and tubes fabricated by the continuous casting processes. The characterisation work for these materials has been important to evaluate and compare continuous casting copper alloy products, and to improve the capacity and performance of the continuous casting process and equipment.

To optimise the casting processes and improve the performance of the mainly cast copper alloys, the following characterisation work has been carried out:

Chapter 1: Introduction

Chapter one will include a brief description and background of the study, problem statements and key aims of the study.

Chapter 2: Continuous Casting

A review of the continuous casting process, machinery, advantages and disadvantages will be discussed.

Chapter 3: Literature Review (Grain Refinement of Continuous Cast Copper Alloys: A Review of Chemical, Thermal and Mechanical Methods)

The findings of Chapter 3 are central to this project. This chapter will present a brief review of grain refinement techniques of continuously cast copper alloys, a comparison of thermal, chemical and mechanical methods and their advantages and limitations. These will provide useful information to gain an in-depth understanding of the exact effect of grain refinement techniques on the physical and mechanical properties of continuously cast copper alloys which will provide pointers to future research directions.

Chapter 4: Experimental Devices and Instruments

In Chapter 4, the main analysis and measurement tools which this project utilises are introduced. Although many of these techniques are standard scientific tools, they are important to explore and understand the mechanism and physical principles. Metallography sample preparation, digital optical microscope, SEM/EDX, tensile machine and spectrometer are explained separately.

Chapter 5: Copper Tubes

The main purpose of this chapter is to compare the physical and mechanical properties of DHP (deoxidized high phosphorus) copper tube samples prepared by various industrial processes such as casting, drawing and annealing, planetary rolling and extrusion. The average grain sizes of these samples were investigated according to standard ASTM E112 using a Planimetric procedure and a new method, which will be hereby referred to as the "total grain counting method". Mechanical properties of continuous cast DHP copper tube have been carried out by a drift expanding test.

Chapter 6: Copper Rods

In Chapter 6, an investigation was carried out to understand the effects of various solidification parameters on the physical and mechanical properties of continuously cast copper rod. In the present work, the impact of some effective parameters on the tensile strength and elongation percentage of copper alloys fabricated by continuous casting technology were investigated. These parameters were: (1) water flow rate, (2) casting speed, (3) alloying element, (4) pull distance, (5) melt temperature, (6) cleanout cycle, (7) continuous casting direction and (8) super-cooler size.

Chapter 7: Effect of Antimony Addition Relative to Microstructure, Mechanical Properties and Rod Surface Finish of Continuously Cast Lead Alloy

The aim of this chapter was to investigate the physical and mechanical properties of the addition of (1.25%wt) antimony (Sb) to lead (Pb). The continuous casting process was applied to a Pb and Pb1.25%Sb alloy, in order to study the efficiency of alloying elements on microstructure and mechanical properties, as well as to study the relationship between microstructure and mechanical properties of continuously cast Pb and Pb-Sb rod.

Chapter 8: Investigation of the Distribution of Lead in Three Different Combinations of Brass Feedstock

The main objective of this chapter was to investigate the distribution of lead in a new continuously cast leaded-brass alloy (pending application with Copper Development Association - CDA) with three different combinations of brass feedstock.

Chapter 9: Conclusion

The final conclusions of this study and recommendations for future research are in Chapter9.

Chapter 2 - Continuous Casting

In this section, background, applications, procedure and types of of continuous casting are introduced, followed by a review of the main parts of a continuous casting machine.

2.1 History and evolution of Continuous Casting

Whilst the generic process of casting has a history more than 5000 years old, the current techniques of continuous casting is a process that has only been developed properly over the last 50 years or so, However, the process of continuous casting of metals has been practised for well over a century. A review of literature indicate that, apart from the outstanding work by by Sir Henry Bessemer in 1857 at Sheffield UK on steel casting, the first recorded patent in the non-ferrous was in America in 1840, for the manufacture of lead pipes. Sir Henry Bessemer designed his continuous casting machine by casting metal between two contra-rotating rollers for manufacturing metal slabs (Birat J.P, 2004).

Figure 2-1 shows the original drawing of Bessemer which illustrates the principle of producing of metal slabs that is considered to be the first method of continuous casting in the world.

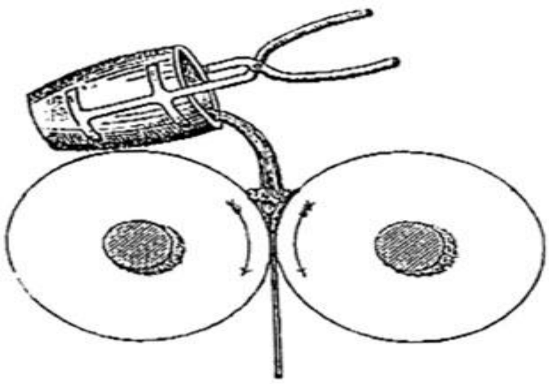


Figure 2-1:Bessemer’s original continuous casting equipment using chilled roller (Birat J.P, 2004)

The first horizontal closed-heat system for continuous casting was developed by a Swedish engineer for the production of cast-iron bars in 1914 and then in 1938 first successful continuous casting machine using graphite as the mould materials designed. Up till now, continuous casting technology has been developed by installation of several robotic applications in different areas of continuous casting machinery, for instance Figure 2-2 shows the robotic steel sampling, Figure 2-3 shows robotic temperature measurement system (Juergen Meisel, 2014) and Figure 2-4 shows automatic copper cathode feeding at Rautomead (http://www.rautomead.co.uk/).

Figure 2-2: LiquiRob installed at LOP for sampling in continuous casting of steel slab (Juergen Meisel, 2014)

Figure 2-3: LiquiRob during temperature measurement at POSCO Gwangyang for temperature measurement in continuous casting of steel slab (Juergen Meisel, 2014)

Figure 2-4: Rautomead RS3000 automatic cathode feeding system (http://www.rautomead.co.uk)

2.2 Application of Continuous Casting

The continuous casting process is a method which is used in manufacturing industry to cast a continuous length of metal. This technique is frequently used in steel, aluminum, copper and other alloy industrial applications to produce a wide range of different profiles such as wire, rod, tube shell, billet and strip. The use of continuous casting gives a range of advantages (cost effective, time saving, high production process that can be fully automated, etc) in comparison to other conventional casting methods (John H. Gibbons., 1979).

2.3 Continuous Casting Procedure

Continuous casting is a process of melting and continuous solidification. As a particular example, as shown in Figure 2-5, Rautomead continuous casting consists of a graphite heating element, heated furnace with graphite crucible furnace and holding furnace, together with graphite die and super cooler assembly with the withdrawal mechanism controlled by PLC (Programmable Logic Controller) based servo motor.

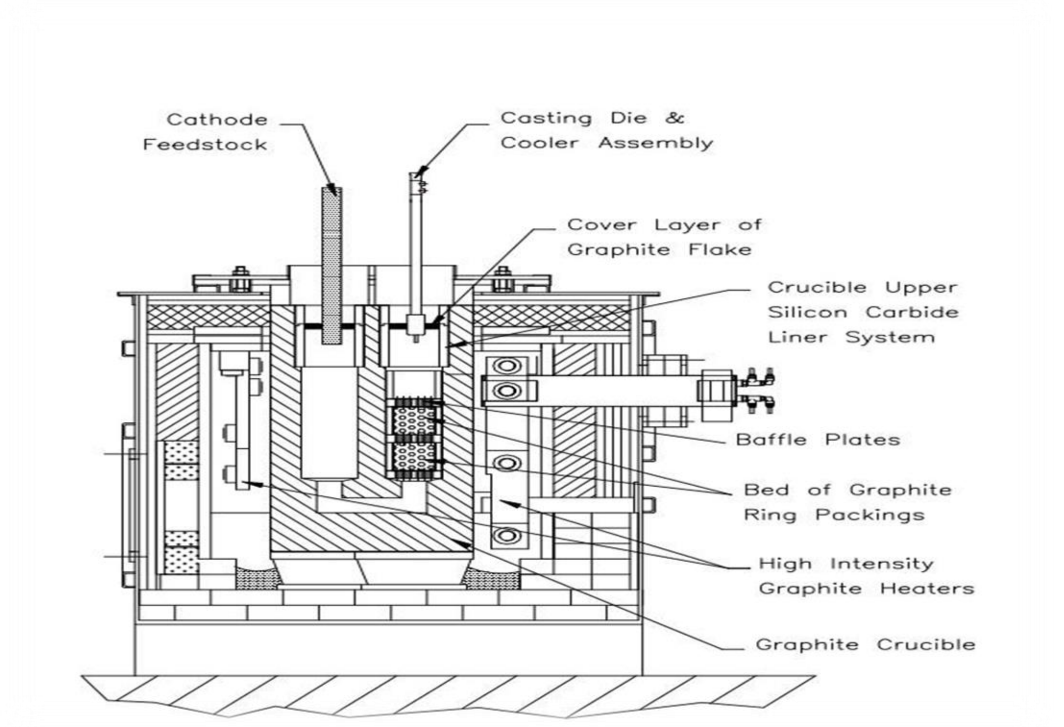


Figure 2-5: Section through rautomead RS upwards vertical continuous casting furnace (http://www.rautomead.co.uk)

2.4 Continuous Casting Types

There are various types of continuous casting machines which depend on material and continuous casting processes, such as: vertical machines, curved machines, horizontal casting , thin strip casting, single roll casting, two roll casting, twin belt casting and rotary casting.

Here are some examples:

- Aluminium alloy for special applications is cast by vertical machines.
- Most steel casting requires bending and/or unbending of the solidifying strand produced by curved machines.
- Horizontal casting is used with both nonferrous alloys and steel.
- To minimize the amount of rolling required, thin strip casting is an alternative method for steel and other metals in low-production markets (Thomas, 2001).

According to material and section size, the continuous casting process of copper alloys to produce round billets for processing extrusion, forging or wire drawing are (Nairn, 2013) and (Wilson, 1999):

- Vertical upwards,
- Vertical downwards
- Horizontal

2.5 Rautomead Continuous Casting Machines

Rautomead Limited was founded by Sir Michael Nairn in 1978. Rautomead Ltd of UK has specialised in the design, manufacture and sale of continuous casting equipment for non-ferrous metals/alloys. Over that period, more than 400 systems have been built and installed at customer sites in 47 countries (http://www.rautomead.co.uk). Rautomead plants are being used world-wide in production of:

1- Oxygen-free copper
2- Copper conductor alloys
3- A wide range of copper-based engineering alloys
4- Gold and silver alloys
5- Zinc and zinc alloys
6- Lead and lead alloys (new project)

Rautomead is a specialist in continuous casting of non-ferrous metals and is well known as one of the best manufacturers of continuous casting technology of:

(a) Upwards casting for wire rod and tube shell
(b) Horizontal casting for billet,strip and rod as well

2.5.1 Upwards Casting for Wire Rod and Tube Shell

The Rautomead vertical upwards casting machines are designed for the processing of dry, clean, bright, flat, un-oxidized copper cathode as the feedstock, free from electrolyte nodules to produce 8.0mm diameter wire rods. This may be designed to produce rods up to 22.0mm diameter depending on customer requirement. The Rautomead vertical upwards casting machines are built to be operated for long periods of continuous production of continuous cast copper wire rod. The Rautomead vertical upwards casting machines (RS small machines as a commercial name) are configured as integrated melting, holding and casting units, featuring graphite crucibles protected in an inert gas atmosphere with high intensity graphite resistance heating. The (RDG large machine as a commercial name) series features large induction furnace technology. Machines are either single furnace integrated melting and casting or dual furnace with cathode melter feeding a holding furnace, depending on production output.

RDG series such as RDG 360 has feature of;

- Up to 32 strand (8-30 mm dia)
- 15,000 to 30,000 tones per year yield
- Up to 3600 (Kg/Hr) output
- Space require about 20m x 50m
- Automatic cathode feed
- PLC control

RS series such as RS 3000 has feature of;

- Up to only 5 strand (8-30 mm dia)
- Up to only 3,500 tones per year yield
- Space require about 20m x 50m
- Automatic cathode feed

- PLC control

Apart of this, Rautomead combine with SMS Meer's Schumag and Copper division to offer a new copper tube manufacturing process. The Rautomead cast tube upward vertical casting process produces copper tube shells that are formed into coils.

The continuous casting technology for thin wall copper tube shells can produce high quality 38mm, 42mm and 52mm outside diameter tubes (new project). RS continuous casting works with Rautomead graphite furnace technology which can be used with the automated cathode feed system. These are subsequently processed on SMS Meer equipment to result in a finished product through a draw machine, annealed, and then drawn.

Finishing equipment is selected according to specific factory requirements (http://www.rautomead.co.uk).

Figure 2-6 shows the schematic of the vertical continuous casting factory and Figure 2-7 shows the actual vertical continuous casting factory.

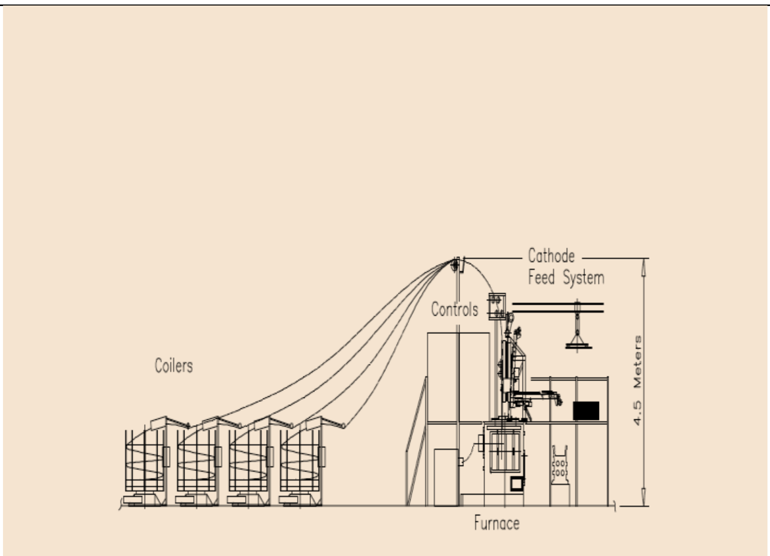


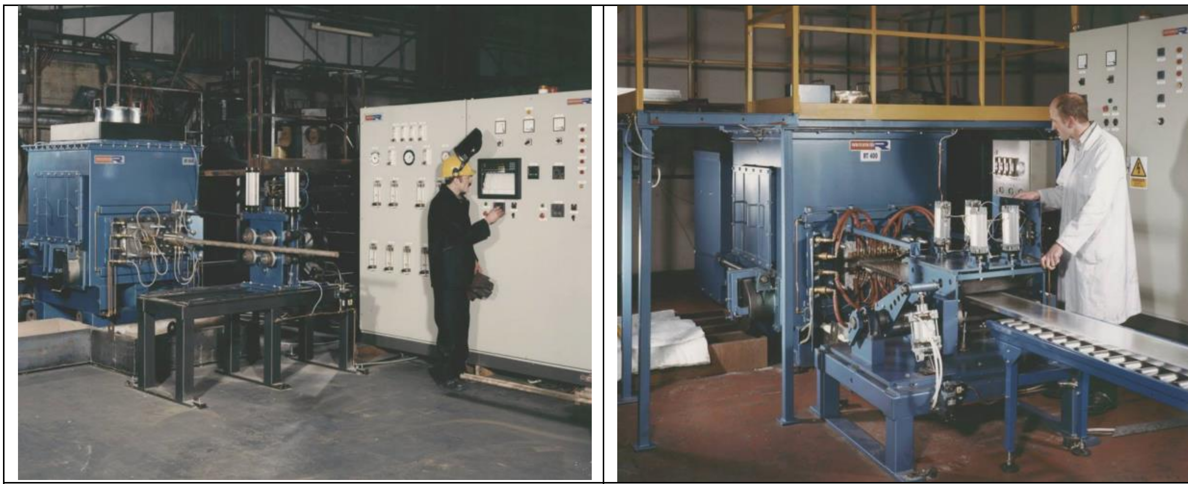
Figure 2-6: Schematic of the vertical continuous casting factory (http://www.rautomead.co.uk)

Figure 2-7: Vertical continuous casting factory (http://www.rautomead.co.uk)

The majority of the analysis covered within this PhD thesis is on material cast vertically rather than horizontally. This is because vertical continuous casting has in general (a) higher casting speed vs horizontal, (b) requires less die change time, (c) has higher production efficiency and (d) is in general a safer process.

2.5.2 Horizontal Casting for Billet, Strip and Rod

The Rautomead Horizontal Continuous Casting Machines are designed for the production of a wide range of copper based engineering alloys such as brasses, bronzes, aluminium bronzes, etc. Rautomead engineering alloy machines may be used either as single furnace integrated melting and casting engineering alloy machines or as holding and casting machines fed with pre-alloyed liquid metals from a primary melting furnace, depending on alloy, section size and desired output (http://www.rautomead.co.uk). Figure 2-8 (a) shows the billet horizontal continuous casting and Figure 2-8 (b) shows the strip horizontal continuous casting.



(a) Billet horizontal continuous casting | (b) Strip horizontal continuous casting

Figure 2-8: Horizontal continuous casting (http://www.rautomead.co.uk)

2.6 Key Advantage of Rautomead Continuous Casting Machine

The advantages of using Rautomead RS series machines are (http://www.rautomead.co.uk):

1- Factory footprint (space): Factory footprint is defined as the shape and size of the area something occupies. For continuous casting machinery, the factory footprint required is dependent on the method of handling of cathode and rod coils. The Rautomead RS series machines are very compact and require little factory floor space. As a particular example, the model RS 2200/8/8 has a footprint of only 15 metres by 5 metres and a height of 4.5 metres. Also for Rautomead machines, no special foundations are required. A normal reinforced concrete floor of 150 mm thickness is sufficient.

2- Environmental considerations: The Rautomead process uses clean resistance furnace and thus is inherently clean. Melting of copper in the system gives off no fumes and no effluent is produced. Sound levels are also normal.

3- Operating hours: The Rautomead RS series machines are able to work seven days a week and not be necessary to stop the machine. However it is recomended to stop the machine for maintenance attention every six months. If, for other reasons, it is necessary to stop the machine, it may be left in "stand-by" mode, with the copper molten in the crucible.

4- Using graphite: The Rautomead continuous casting system is based on electric resistance heating of its furnaces. Rautomead technology for continuous casting is unique because it uses graphite for crucible, dies and heating elements.

Graphite can operate only in a non-oxidising atmosphere. Therefore, crucible and die assembly must be housed in a sealed furnace and protected by an inert gas. Most high grade copper, brass, tin bronze, phosphor bronze, aluminium bronze can be successfully cast in an all graphite crucible/die assembly

Normal cathode copper has oxygen and using graphite could reduce the level of oxygen which is particularly suited for production of high purity, high quality oxygen-free copper and copper alloy wire rods such as copper silver, copper magnesium, copper tin, etc.

2.7 Main Parts of RS Machines:

Usually each continuous casting line consists of one melting furnace and one holding furnace with twin cast strand. Each cast strand shall consist of a separate withdrawal unit, coiler unit, cooling system and power supply along with all accessories. As shown in Figure 2-5, Rautomead continuous casting also consists of a graphite heating element, a heated furnace with graphite crucible furnace and a holding furnace, together with graphite die and super cooler assembly with withdrawal mechanism controlled by PLC based servo motor.

The main components of RS continuous casting machines are as follows (http://www.rautomead.co.uk):

1) Resistance furnace
2) Continuous casting machine
3) Cooling system

4) Electrical control system (control panel)
5) Cathode feed system
6) Coilers.

Figure 2-9 shows the schematic of continuous rod casting machine.

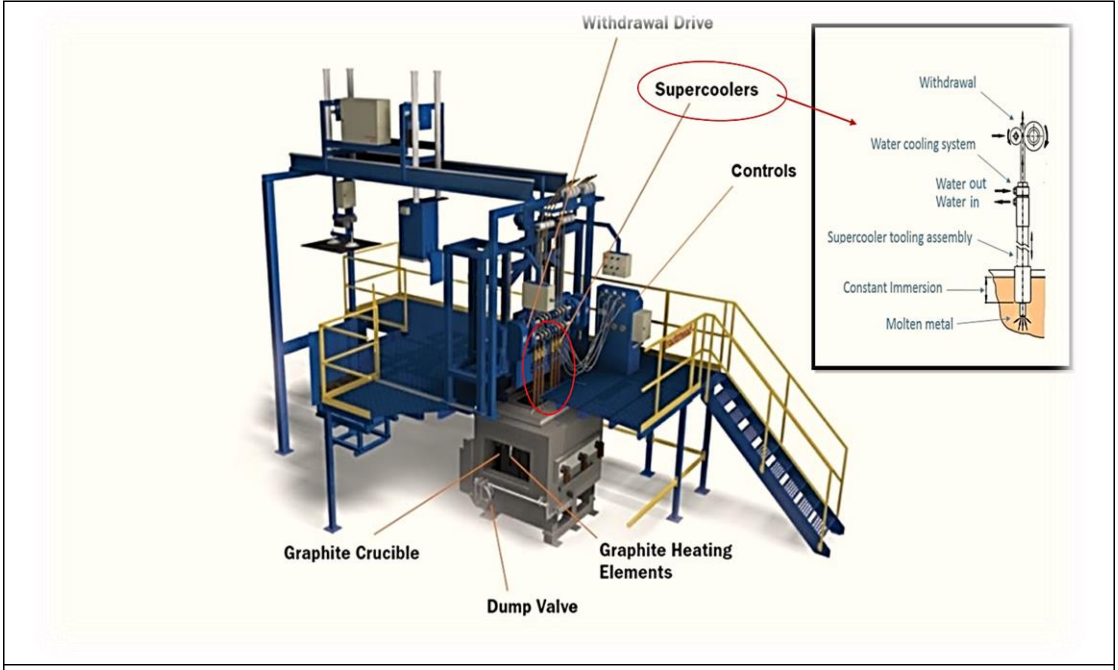


Figure 2-9: Schematic of Continuous Rod Casting Machine (http://www.rautomead.co.uk)

2.7.1 Resistance Furnace

The resistance furnace consists of a furnace body and furnace frame and is used to melt copper cathode or scrap into liquid and keep liquid at a constant temperature. A crucible is a container which is used to hold alloys for melting in a furnace which needs to resist the temperatures in melting metals. The crucible is made by high temperature-resistant materials. These materials can resist the highest temperatures in metal casting work. Graphite crucible can withstand the high temperature, and has good resistance to chemical erosions and thermal shock. The naturally reducing effect of the graphite material assists in ensuring the full de-oxidation of copper and avoids contamination of the melt by refractory particles. These properties makes graphite crucibles well suited for use in the melting of copper alloys. (P.Prabhakara Rao, 2014) , (Percy, 1861) and (Nairn, 2013). Figure 2-10 shows the Rautomead graphite crucible.

Figure 2-10: Rautomead graphite crucible (http://www.rautomead.co.uk)

2.7.2 Graphite Heating Elements

Graphite has long been used as a heating element. For melting of some metals, it is necessary sometimes to provide temperatures up to 2,000 C. Graphite has a low expansion coefficient. Graphite materials also get stronger while their temperature increases. So the graphite can operate at over 2000 °C. Apart from this, the good electrical conductivity of graphite allows the graphite to be used as heating elements in a low voltage resistance furnace heating system. 450 kWh is the power required for melting and casting Key features of Rautomead technology are using of graphite crucibles and electric resistance heating elements. These features makes Rautomead different from almost all of their competitors. Graphite resistance heating elements are positioned around the crucible. By suitable element design, heating can be biased towards any particular area such as melt zone and die entry. (F., 1990) and (Patent No. US Patent US 3395241 A, 1968) and (Nairn, 2013). Figure 2-11 illustrates the rautomead graphite heating elements

	
(a) Instalation of the heating elements	(b) Heating elements

Figure 2-11 Rautomead graphite heating elements (http://www.rautomead.co.uk)

The heart of a continuous casting machine is the die. The die is an open-ended tube in which the metal is poured. The most important parameters which determine the choice of the die material are: the composition of the alloy to be cast, the casting orientation (vertical or horizontal), the size and shape of the cast section, the speed of casting, and the total amount of alloy to cast.

The main characteristics that the casting die must have are the following: high thermal conductivity, good machinability, long life, wear and tear resistance, a high melting temperature, thermal shock resistance, thermal stability, low heat capacity, low friction coefficient and must have high resistance to burn-out and tension. According to all of the previous characteristics, the material used generally to manufacture the casting die is graphite. The key features of graphite, such as increased strength at higher temperature, high thermal conductivity, high thermal shock resistance, good electrical conductivity, non-wetting, easy machined, relativity soft, high lubricity and porosity all which make graphite die suitable for the continuous casting of high grade copper. (Rodriguez, 1999).

As a particular example, in production of 8mm dia, oxygen free copper rod, graphite casting die inserts can be expected to produce around 12 tonnes of rod which represent 'lifespan' of graphite die. (Nairn, 2013).

Figure 2-12 shows the Rautomead graphite die.

Figure 2-12: Rautomead graphite die (http://www.rautomead.co.uk)

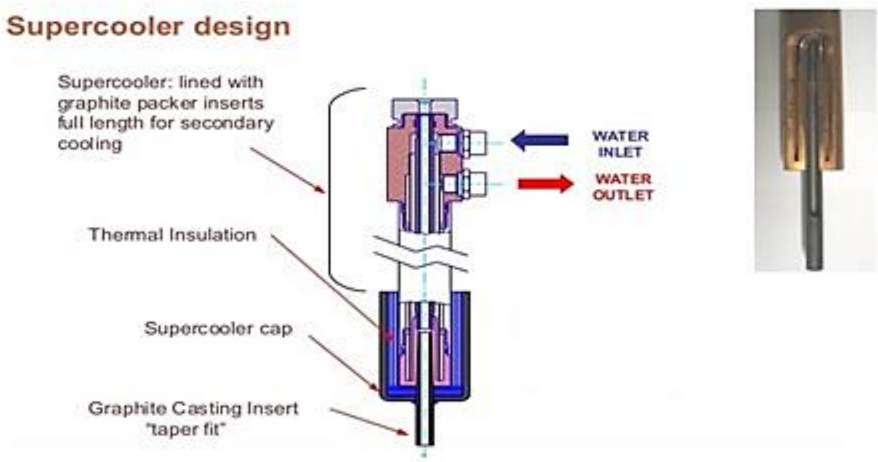
2.7.3 Continuous Casting Withdrawal System

A continuous casting withdrawal system, which is the main part of the system, consists of a drawing mechanism and a mechanism of solidification.

The drawing mechanism is made up of A.C. servo motor, drawing rollers, pinchroll, transporter and strands. This part can draw up the copper rod continuously by the drawing rollers.

2.7.4 Cooling System

Casting should be sufficiently cooled to room temperature before its entrance into the withdrawal unit. So, super-cooler is the most important part of a continuous casting machine. It is mounted on top of the holding crucible. The super-cooler is cooled by re-circulation of water. During the continuous casting, the molten metal enters the die and solidifies in the shape of die bore. Figure 2-13 shows the schematic of super-cooler assembly.



(a) Super-cooler Design

(b) Super-cooler Prepration

Figure 2-13: Schematic of super-cooler assembly (http://www.rautomead.co.uk)

2.7.5 Electrical Control System (Control Panel)

The electrical control system can control all the main components of RS and RDG continuous casting machines including a melting furnace system and a holding furnace system, a main machine, a cooling water system, a withdrawal system and cathode feed system (if available).

2.7.6 Cathode Feed System

The cathode feed system can charge whole piece of copper plate into the furnace.

Cathode feed system usually automatic with manual feed for lower outoputs and for cathode types not suited to automatic feeding.

2.7.7 Coilers

Coilers are provided as standard equipment to coil the product into well ordered layered coils of wires and/or tubes. Coils may be handled by forklift truck for final packing process.

2.7.8 Withdrawal System

The withdrawal cycle in continuous casting is introduced by Haissig and Voss-Spilker and Reichelt in 1984 (Haissig, 1984) and (VOSS-SPILKER, 1984).

As shown in Figure 2-14, in vertical & horizontal continuous casting process, generally four different withdrawal cycles are used including (Kopeliovich, 2012):

- Non-intermittent extraction; this regime is generally used for casting alloys with low temperature interval of solidification (eg. pure metals) and in casting at high cooling rate.
- Intermittent extraction with a pause; this regime is used for casting at lower cooling rates. The withdrawal cycle consists of a forward stroke followed by a pause. During the pause the portion of the melt entered the mold starts solidification forming strong skin, which will not tear in the next extraction cycle.
- Intermittent extraction with one pushback; The alloys having wide temperature interval of solidification are withdrawn by this regime. The skin formed during the pause is not strong enough therefore it tears during subsequent cycle. The reverse step followed by the forward stroke causes closing and healing the tears (cracks).
- Intermittent extraction with two pushback; This regime is used for casting alloys containing constituents penetrating into the graphite pores and causing sticking the

casting to the graphite surface. The second reverse step following after the solidification pause results in disconnecting the stuck casting from the graphite. The second reverse step is immediately followed by the next forward stroke.

Hence;

- Acceleration is the time from rest to reach full motor speed.
- Pull is the time taken to cover a pre-set pulse length.
- Decceleration is the time from the end of the pulse plateau to rest and is same as acceleration.
- Total time represent the times acceleration, pull time and deceleration.
- Pulse length is the length in mm travelled in total time and is variable.
- Dwell is the dwell period between cycles.
- Push back is the time taken to cover a pre-set push back pulse period
- Push back cycles is the number of cycles between push back
- Over dwell covers a periodic superimposed dwell
- Over dwell cycles is the number of cycles between overdwell

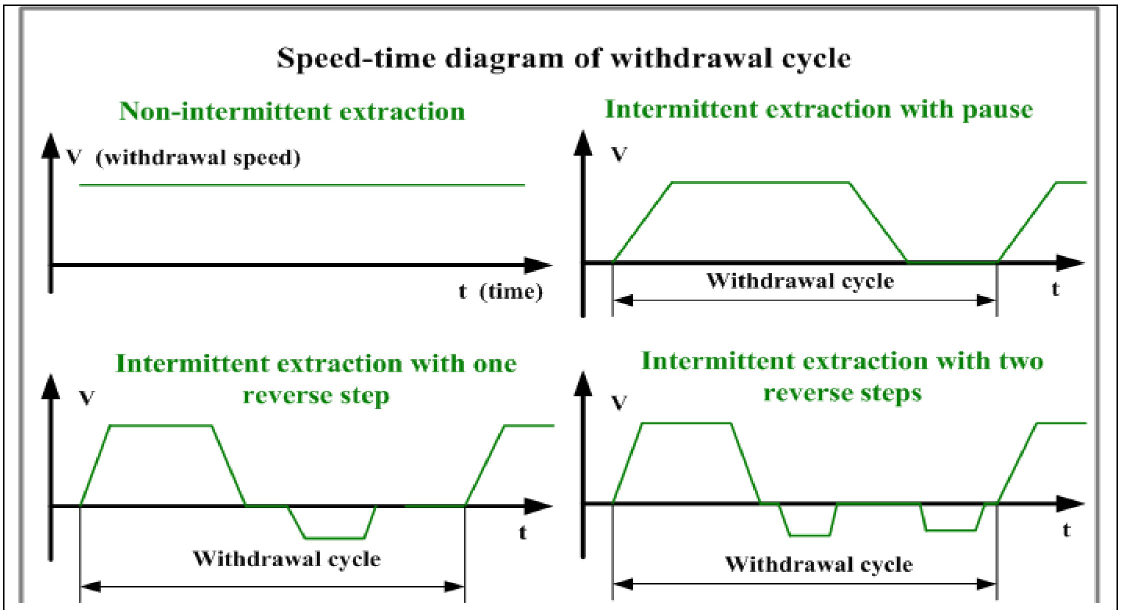


Figure 2-14: Withdrawal cycles (Kopeliovich, 2012)

2.8 Advantage and Disadvantage of Continuous Casting

The major advantages of continuous casting process over other methods are:

- Cost
- Less process
- Maintenance
- Labour cost
- Significant energy saving
- Less scrap produced
- Reduced capital investment
- High production flexibility
- Long size of final product

Although the continuous casting process has many advantages over other manufacturing processes, the literature and the author's experiences have shown that this process has the following limitations (Xintao Li et al 2007):

- Large average grain size (the average diameter of individual grains) as the size of grains affects the strength of any material
- Less elongation and draw ability
- Oscillation marks and crack on surface
- Not suitable for small quantity production

The grain refinement is one of the most effective mechanism, improving the mechanical properties of alloys. In the next chapter, grain refinement techniques are investigated and discussed.

Chapter 3 – Literature Review

Grain Refinement of Continuous Cast Copper Alloys: A Review of Chemical, Thermal and Mechanical Methods

In this section, alloy solidification and grain refinement theory are introduced, followed by a review of grain refinement process for copper based alloys.

3.1 Background

Copper is one of the oldest known metals. It can be used in various ranges of applications such as electronic devices, electrical wiring, cables, refrigeration tubing and plumbing, due to the beneficial characteristics such as excellent heat conductivity and electrical conductivity, good corrosion resistance and good machinability (Joseph, 2001) and (The Copper Tube Handbook, 1995).

Globally, one million tons of copper metals each year are produced by the continuous casting process (T.R.Vijayaram, 2013).

The continuous casting process has several benefits compared to the thermo-mechanical process, including factory footprint size, maintenance, scrap rate, and lower cost and high production flexibility.

One of the major limitations of continuous casting methods is the difficulty in achieving fine and uniform microstructure across the sample and good mechanical properties (Derek E. Tyler & Richard P. Vierod, 2008).

Strengthening is the ability of a metal to deform plastically depends on the ability of dislocations to move. Strength is related to how easiliy a metal plastically deform. So, by reducing the dislocation movement, the mechanical strength can be improved. However, In general mechanism of strengthening in metals are;

- Solid solution strengthening, by adding of one or more materials can increase the strength of metals. Solute atoms, on case of substitunal solid solution create stress fields around themselves and hinder the dislocation movement.
- Grain size strengthening; grain boundaries barrier to slip each others
- Strain hardening (cold working) such as further down process after casting such as forging, rolling, drawing or Equal Channel Angular Pressing (ECAP)
- Heat treatment such as annealing, quenching

In continuous casting, further down process and heat treatment are help to improve the tensile strength or ductility of materials. However, grain refinement techniques have been reported to improve the mechanical properties (ductility or tensile strength), improve surface finish and refine grain structure of copper alloys.

These techniques are effective in refining the matrix, improving the morphology and distribution of the second phase, reducing hot tearing susceptibility, shortening homogenization time, and enhancing mechanical properties. It is well documented that the major benefits of grain refinement process are improved distribution of porosity, feeding, fluidity, surface finishes, machinability, and mechanical properties (Zhiming Yan, 2013) , (Zhao-hui Wang, 2005) and (McCartney, 1989).

The refining of microstructure of metallic materials has been studied by many researchers in the field of metallurgy and metal casting. In fact, key alloy properties such as (a) mechanical properties (b) formability (c) machinability are dependent on the size of the grains in the microstructure (Joo, 2003).

The grain refinement techniques for the continuous cast copper alloys have been an active research topic over past years. The history of grain refining technique dates back to the early 1930s, when foundrymen began to use titanium additions to improve the structure of their castings (Sigworth, 2007). The fine grain process development program began in 1975 to produce a fine, equiaxed grain structure with a vacuum-cast IN713LC radial turbine wheel (M. Would, 1984). Since the 1980s, there have been various grain refining techniques developed; this research is ongoing. Currently, methods of grain refinement used in the casting process are mainly classified into the following methods (T. Robert et al, 1992):

1- Chemical method by addition of grain refiners
2- Thermal methods such as cooling rate control
3- Mechanical methods such as agitation of melt during solidification

In this chapter, the advantages and limitations of these three methods will be explored, especially in terms of cost benefits and equipment requirements.

3.2 Review of Grain Refinement Techniques

Control of the solidification microstructure is one of the most important acts in copper alloys which directly and indirectly influence the mechanical performance. In the majority of cases, a fine and small microstructure is beneficial, improving mechanical properties and surface finish which means that, alloys with smaller grains exihibit enhanced mechanical properties.

Therefore, grain-refinement in copper alloys has recently raised considerable interest from the research community.

It is generally known that mechanical properties of alloys have correlation with grain size and superior mechanical properties are achieved by small grain structure (Campbell J. , 1991).

The Hall-Petch equation explains the correlation between grain size and yield strength which is defined as the stress where deformation changes from being mostly elastic to mostly plastic. (William D. Callister, 6th edition - 2003):

$$\sigma_y = \sigma_0 + K_y d^{-½}$$

Where:

σ_y = yield strength

σ_0 = friction stress, representing the overall resistance of the crystal structure to dislocation movement

Ky = locking parameter, measuring the relative hardening contribution of grain boundaries (material parameter)

d = average grain diameter

The solidification of any molten metal occurs by nucleation and growth which means the two distinct mechanisms of grain size control are nucleation and growth restrictions. Nucleation appears in the molten metal in the form of tiny solid particles called nuclei, when phase transformation in the metal occurs.

These nuclei are created from the deposition of atoms and grow into the form of crystals and become completely solidified grains. So, the grain size is controlled by (a) crystal nucleation and (b) crystal growth.

The process of nucleation and growth occurs in two different stages. In the first stage, a small nucleus is created and then in the second stage crystal growth spreads outwards from the nucleating site (Nanev, 2015).

3.2.1 Nucleation Theory

In order to understand the principles of grain refinement techniques, grain nucleation theory must be discussed. Nucleation is a process of formation of a stable crystallisation centre of a new phase. Nucleation, the creation of a new crystal phase in the body of the mother phase, is one of the most fundamental aspects of phase transition in general and crystal growth in particular. Depending on the value of undercooling of the liquid phase , nucleation may occur by (a) a homogeneous mechanism (without the influence of foreign particles) or (b) heterogeneous (with the influence of foreign particles) (Gruzleski, 2000).

3.2.2 Homogenous Nucleation

This section explains homogeneous nucleation (the simplest nucleation process) of solid crystals during the freezing of a pure metal. Solidification with a high degree of undercooling is characteristic of homogeneous nucleation.

In alloys, commencement of solidification is easy since the foreign atoms act as source of nucleation but pure metals experience difficulties in commencing solidification (there are no foreign atoms to form nuclei). In case the metal cools below its freezing temperature and actual solidification begins at the same point as illustrated in Figure 3-1. Supercooling also known as undercooling is the process of lowering the temperature of a liquid below its freezing point without it becoming a solid.

In fact, if a metal is 100% pure and contains no traces of other elements then some undercooling may occur before solidification begins. Undercooling is when the temperature drops below the liquid to solid temperature for a short period.

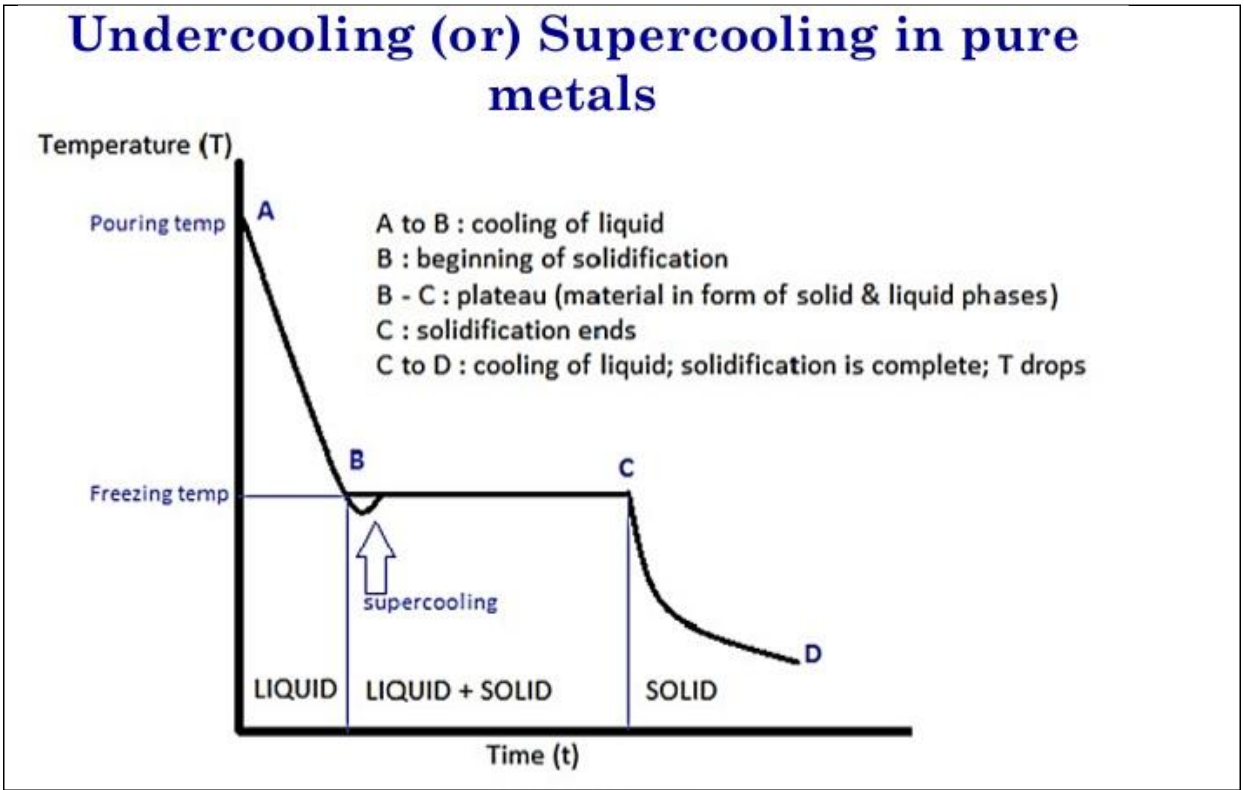


Figure 3-1: Solidification process of liquid metal with undercooling (Gruzleski, 2000)

3.2.3 Heterogeneous Nucleation

Heterogeneous nucleation theory involves nucleation from a foreign particle in the melt such as grain refiners. Presence of foreign particles in the liquid alloy allow crystallisation to initiate at a minor value of undercooling. This is heterogeneous nucleation. So, the main aim of using grain refiners is to act as particles in the melt, which enhance the probability of heterogeneous nucleation (Loper C.R & Kotschi R.M, 1974). Solidification with no undercooling is typical of heterogeneous nucleation, which is shown in Figure 3-2.

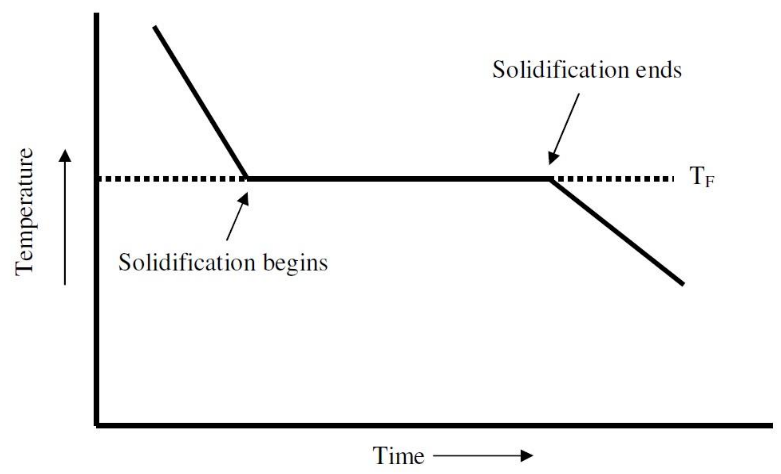
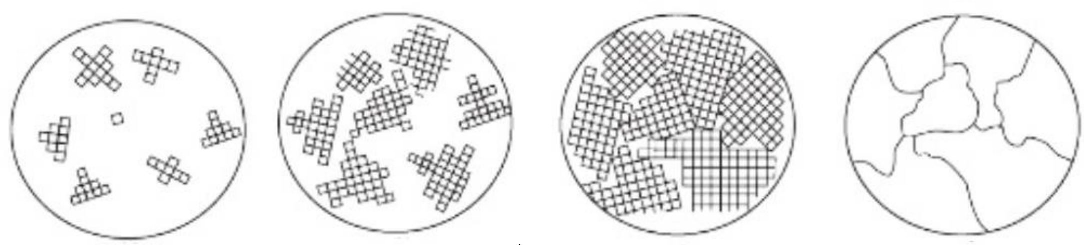


Figure 3-2: Solidification process of liquid metal without undercooling (Loper C.R & Kotschi R.M, 1974).

Heterogeneous nucleation occurs much more often than homogeneous nucleation.Heterogeneous nucleation is typically understood to be much faster than homogeneous nucleation using classical nucleation theory. This predicts that the nucleation slows exponentially with the height of a free energy barrier. This barrier comes from the free energy penalty of forming the surface of the growing nucleus.

3.2.4 Crystal Growth

Crystal growth is the process of phase transition from a liquid to a solid. At the solidification temperature, atoms from the liquid bond together and then start to form a crystal. After that, a crystal begins to grow and while a metal begins to solidify, multiple crystals begin to grow. The final size of the individual crystals is dependent upon the number of nucleation points. At the final stage, a grain boundary will form. During the growth stage the nuclei increase in size, which results in the disappearance of some or all of the parent phase. The transformation reaches completion if the growth of these new phase particles is allowed to proceed until the equilibrium fraction is attained. Figure 3-3 illustrates the schematic of the four stages during solidification of molten metal (Makio Uwaha, 2015).



(a) Nucleation of crystals	(b) Crystal growth	(c) Crystals grow together	(d) Grains and grains boundaries

Figure 3-3: Schematic of the four stages during solidification of molten metal (Makio Uwaha, 2015)

The main goals of this chapter are to:

- Discuss the effects of the addition of the nucleant agents and nano-particle grain size refiner additions, preparation of nanoparticles, and grain refining procedures.
- Study the efficiency of the thermal grain refining technique on the physical and mechanical properties of alloys.
- Investigate the mechanical methods and discuss the mechanical agitation of melt during solidification.

The above parameters are explained from section 3.3 to 3.5.

3.3 Chemical Method

Grain refinement by chemical method involves the addition of elements nucleation and the process of hindering growth. Chemical method, by adding chemical powder, is an effective technique. But still, grain refiners as foreign particles, have their own limitation.

Below, grain refiner types and their characteristics and properties will be introduced. The section concludes that chemical methods require careful consideration of many different phenomena to produce continuous cast fine grain structure and acceptable ductility copper alloys (Joo, 2003).

3.3.1 Grain Refiner Properties

By adding grain refiners that increase the number of nucleation sites, it is possible to develop fine grains in as-cast structures and improve the strength of alloys (McCartney, 1989).

Processing, properties and applications of chemical grain refiners have been extensively investigated in the past decades, such as phosphide, silicon, TiB_2 or tungsten carbide and so on. Currently, interest is growing in producing components refined by grain refiners by adding these particles to liquid metals (M.X. Guo, 2008) and (El-Mahallawi et al, 2010). An effective nucleant grain refiner must have the following characteristics (BS Murty, 2002):

1) Similar crystallographic planes and good wettability

2) Generally melting point higher than the alloy being solidified

3) An ability to initiate freezing at a very small undercooling

4) Sufficient nucleating sites that are distributed uniformly

5) The particle size should be larger than the critical radius. Minimum size that must be formed by atoms or molecules cluster together before a new phase solid particle is stable and begins to grow.

3.3.2 Grain Refiner Types

Grain refinement techniques are classified into 3 types (Loper C.R & Kotschi R.M, 1974):

1) Slow acting, in which the optimum contact time is long

2) Fast acting and early fading, in which the optimum contact time is short
3) Fast acting and long lasting

The ideal grain refiner has these characteristics and at present this chemical refinement is widely used. Figure 3-4 shows these three grain refiners.

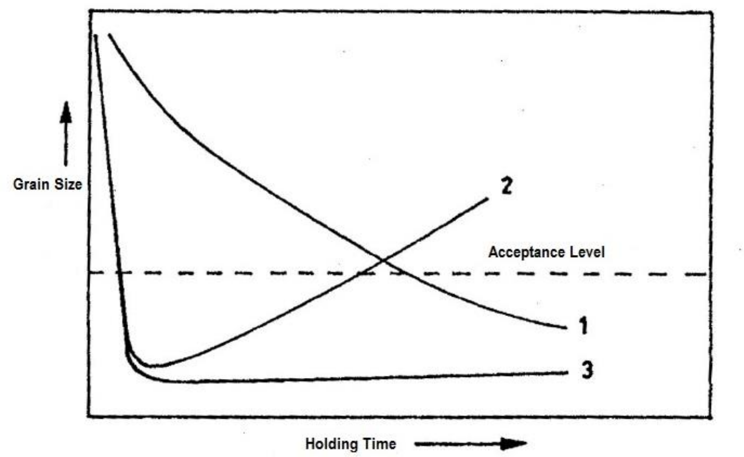


Figure 3-4: Typical form of grain refiners (Loper C.R & Kotschi R.M, 1974)

As can be seen in the case of number (1), acting of the grain refining process is slow, which is not useful for the grain refining goal. As can be seen in the case of number (2), by increasing time the grain size will be increased. This is due to dissolution of the nucleating site or floating of the grain refiner because of differences between density of grain refiner and the melt. Hence type (3) is mostly used (BS Murty, 2002). In this figure, acceptance level is a level of encourages fine grain formation.

3.3.3 Nano-Particle Grain Refiner

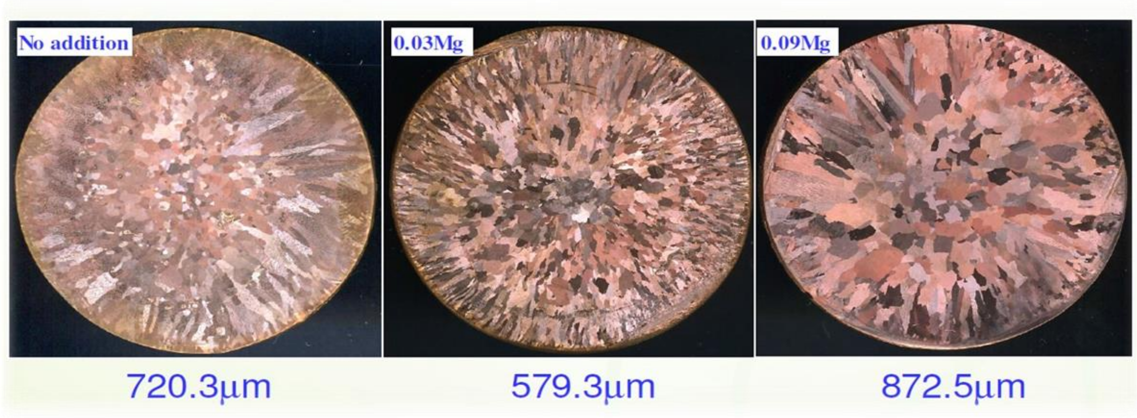
The approximate size of the nanoparticles is between 10 and 100 nm (J. Ružić, 2012) and (Patent No. CA2599440 A1, 2006).

At the present time the nanoparticles are produced by intricate sophisticated techniques e.g. laser-induced pyrolysis, laser evaporation and condensation, plasma torch synthesis, deposition from colloidal solutions, reduction from aqueous solutions, crystallisation from amorphous solid phase, etc (Stefan NIŽNÍK et al 2011). Nano-particles could be wrapped in copper foil and then incorporated into the molten metal.

3.3.4 Limitation of Chemical Grain Refiner

The literature and the author's experiences have shown that the chemical grain refining process has the following problems (M. Would, 1984) , (Mondolfo, 1983) , (T. Robert et al 1992) and (Kim, 2010) and (BCAST, 2013):

- The amount of refiner: Figures 3-5 to Figure 3-7 show the etched as-cast grain structure for the base alloy and the grain refined casting for all addition levels. A listing of all measured grain sizes are presented in Table 3-1. This table and the following figures showed that, the grain size of copper alloys (without the addition of a grain refiner) was 720.3 μm and as a particulat example an addition of a small amount (0.2wt %) of MgO particles almost halves the grain size of copper, with the average grain size being reduced from 720.3 μm to 392.9 μm. In other hand, the grain structure of the copper alloys (with the addition of 0.09 (wt %) Mg) was highly coarse and the average grain size being increased from 720.3 μm to 872.5 μm.
- Difference in density between matrix and refiner. As a particular example due to the markedly different density between Cu (8.96 g/cm^3) and MgO (3.58 g/cm^3), MgO isn't an efficient grain refiner to DHP Cu. The density of TiB_2 is 4.52 g/cm^3, so TiB_2 at a concentration of (~1 wt. %) is an efficient grain refiner to Cu.
    - Lack of uniform dispersion of nucleant agents.
    - Poor wettability or incompatibility between metal and oxide particles



(a) As cast copper rod without grain refiner	(b) The grain structure of as cast copper rod with addition of 0.03(wt %) Mg as a grain refiner	(c) The grain structure of as cast copper rod with addition of 0.09(wt %) Mg as a grain refiner

Figure 3-5: Addition of pure Mg (BCAST, 2013)

(a) As cast copper rod without grain refiner	(b) The grain structure of as cast copper rod with addition of 0.06(wt %) Mg oxide as a grain refiner	(b) The grain structure of as cast copper rod with addition of 0.2(wt %) Mg oxide as a grain refiner	(b) The grain structure of as cast copper rod with addition of 0. 6(wt %) Mg oxide as a grain refiner

Figure 3-6: Addition of MgO (BCAST, 2013)

Table 3-1: Average Grain Size vs Inoculation addition (wt %) (BCAST, 2013)

No	Inoculation addition (wt %)	Mean grain size, µm
1	No Addition	720.3
2	0.03 Mg	579.3
3	0.09 Mg	872.5
4	0.06 MgO	431.5
5	0.20 MgO	392.9
6	0.60 MgO	425.6

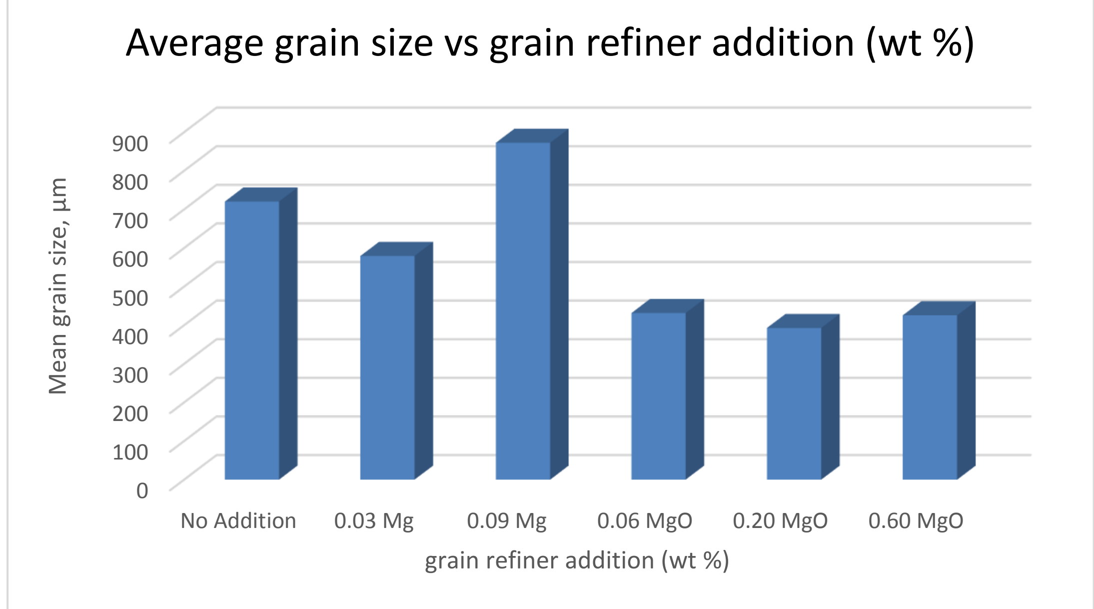


Figure 3-7: Average grain size versus inoculation addition (wt %) (BCAST, 2013)

As shown in the above graphs, MgO could be classified as a grain refiner but pure Mg cannot. This is because the melting temperature of Mg is less than that of pure copper.

3.4 Thermal Method by Controlling the Cooling Rate

Thermal method, which is a grain refining process intended to increase the casting quality, involves rapid cooling and variation of process variable (Joo, 2003).

This method was proposed by a Russian researcher and then studied by Japanese and Chinese researchers; this research is still valid (Jun Wang et al, 2003). In this section, the theory of cooling rate is introduced, followed by a review of the efficiency of cooling rate on grain structure of continuous cast copper alloys.

The section concludes, thermal method is an economical process which is used to produce continuous cast fine grain structure and acceptable ductility copper alloys. In the next chapter, the author attempts to report seven methods which produce continuous cast copper rods with better mechanical properties.

3.4.1 The Fundamentals of Cooling Rate

A very important aspect of study is the problem of shaping structure during the casting process. This can be done by skilfully controlling the cooling conditions. The thermal method is a known method to produce metals with small grains by controlling the cooling rate. When the cooling rate is slow, some of the large clusters of atoms in the liquid develop interfaces and become the nuclei for the solid grains which are forming. During solidification, the first nuclei increase in size as more and more atoms transfer from the liquid state to the solid state.

Eventually all the liquid transforms and large grains develop. The grain boundaries represent the meeting points of growth from the various nuclei initially formed. When the cooling rate is fast, many more clusters develop and each grows rapidly until it meets its neighbour. As a result more grains form and the grain size in the solid metal is finer. Therefore the final grain size of a metal depends to a great extent on the rate of cooling. When the rate of cooling cannot be controlled, eg in the centre of large castings, a fine grain size can be achieved by introducing nuclei into the liquid metal to begin more numerous sites for crystal growth.

This technique is known as the thermal grain refinement technique and is of great importance for producing metal castings that are to be used in their cast condition, since grain size has so much influence on the mechanical properties. The effect of cooling rate on the structure of the continuous cast copper alloys are illustrated in the following Figures. It must be noticed that fine grains can be achieved by increasing the casting speed, as seen in these Figures.

Figure 3-8 presents the microstructure morphology of cross section as cast samples, and the results of the effect of cooling rate on longitudinal sections of continuous cast copper alloys is presented in Figure 3-9.

In this figure, longitudinal and cross sections of Cu-OFE grade rods cast at ten different speeds. The materials exhibit a structure that is typical for classic castings, i.e., for copper cast with high speeds in a range from 0.5÷4.0 m/min., a clear structure of equiaxial grains and a zone of column crystals perpendicular to the axis of the cast material are distinguishable.

Furthermore, analysis of longitudinal sections indicates that the lower the casting speed, the larger the grains found in the castings. Special attention should be paid to the fact that these grains change their orientation from perpendicular to the rod axis, for materials cast at high speeds, to parallel to the rod axis for materials cast at low speeds. It was observed that the material, for which the lowest casting speed was used, exhibits a two to three grain structure of arbitrary length, since this a process of constant casting. When casting speed was increased from 0.006 m/min to 4 m/min, significant improvements of metallurgical properties were observed. With the increasing of the casting speed, the grain structure tends to become finer (William O Alexander, Bradbury E. J. 1985) and (Tadeusz Knych et al, 2011).

4.0 m/min	3.0 m/min	2.0 m/min	1.0 m/min	0.5 m/min	0.2 m/min	0.15 m/min	0.06 m/min	0.03 m/min	0.006 m/min

Figure 3-8: Cross section versus the casting speed (Tadeusz Knych et al, 2011)

4.0 m/min	3.0 m/min	2.0 m/min	1.0 m/min	0.5 m/min	0.2 m/min	0.15 m/min	0.06 m/min	0.03 m/min	0.006 m/min

Figure 3-9: Longitudinal section versus the casting speed (Tadeusz Knych et al, 2011)

3.4.2 Limitation of Cooling Rate Control

The literature have shown that once the casting speed is highly increased it results in a casting fracture. Thus, at high casting speed, casting speed changing should be avoided or a slower rate of speed changing adopted in continuous casting.

3.5 Mechanical Method

Mechanical agitation of melt during solidification is considered one such alternative that has proved to be effective in grain-refining of general casting. The mechanical methods of grain refinement generally involve the agitation of the melt. In this section, fundamental and related techniques of mechanical methods of grain refinement of continuous cast copper alloys are presented. These are more expensive techniques of grain refinement compared to thermal or chemical methods.

3.5.1 The Fundamentals of Mechanical Method

Generally mechanical refining method involves agitation of the molten metal during the solidification process, which requires special devices and increase the cost is usually applied to semi-solid metal processing due to high processing cost (Joo, 2003).

A number of researchers have studied the effect of this technique on mechanical properties and microstructure changes of as-cast samples. They all have reported an enhancement in the alloy grain structure that consequently can improve the mechanical properties of the alloys. They conclude that grain refinement of alloy is possible with this method without addition of chemical additives. The mechanical grain refinement methods involve promoting nucleation, dispersion and multiplication of solidified crystals under mechanical force without any further chemical additions. Mechanical grain refinement generally creates a favourable condition for nucleation and nuclei survival or breaking the solidified crustal structure (L. Zhang, 2012) , (X. Jian H. X., 2005).

3.5.2 Mechanical Method Techniques

However the mechanical grain refinement method is expensive and mainly works for some special casting technology, but there are a number of methods available in order to refine grain size by this technique. Mechanical grain refinement through the external force applied to make fluid flow throughout solidification in order to refine the grain size, such as (Faraji Masoumeh et al 2010) , (Vives, 1998):

- Mould vibration (mechanical vibration, ultrasonic vibration, electromagnetic vibration)
- Stirring of the melt (mechanical or electromagnetic stirring)
- Rotation of the mould
- Rheocasting

Under all these techniques, the grain structures of continuous cast copper alloys can be refined. In this section, these techniques are reviewed and discussed to provide a better understanding of the grain refinement processes.

3.5.2.1 Mould Vibration

Mould vibration techniques such as mechanical vibration, ultrasonic vibration, electromagnetic vibration are used to improve microstructure and mechanical properties of castings by way of grain refinement. In these techniques, moulds or work pieces are held tightly on a vibratory table and the table is tightly attached to the vibration exciter which generates vibrations at different frequencies and transmits them to the table and moulds or work pieces, which in turn vibrate at different frequencies of oscillation. The molten metal solidifies under these vibratory conditions.

A number of examples can be found in the literature which demonstrate that mechanical, ultrasonic and electromagnetic vibrations during solidification of molten metal may reduce the size of grains. It was also noted that by using this technique, the mechanical properties such as tensile strength, hardness, and elongation can be improved as compared to castings without vibration. Furthermore, the literature shows that vibration has a number of other important effects such as an increased density, reduced shrinkage, size and distribution of second phases. (Campbell J. , 1981) and (Verma et al, 2011). This method is very expensive.

3.5.2.2 Stirring of the Melt

Mechanical and electromagnetic stirring are known to achieve grain refinement in solidification processes. By using this method, the mechanical properties of continuously cast copper alloy are enhanced by the application of an electromagnetic field. On the other hand, grain structure of copper alloys can be refined. However, most of the previous experimental results have been difficult to apply in mass production. The previous study has also shown that this method is not suitable for a large-size product of the material because of a complicated procedure as well as higher cost. The results are dependent on input current (Xintao Li et al, 2007) and (Xintao Li & Tingju Li, 2005).

3.5.2.3 Rotation of the Mould

A number of examples can be found in the literature where rotation of the mould has been applied during solidification in order to refine grain size. This technique is simpler than any semisolid processing like rheocasting. This method is also easier and more economical than ultrasonic and electromagnetic methods (X. Jian T. M., 2006) and (L. Zhang, 2012) but the results are dependent on rotation speed. This method is mainly used for steel or horizontal casting.

3.5.2.4 Rheocasting

Rheo-processing is a semi-solid process which has also been used as a grain refining technique. Rheocasting is a new technology for manufacturing of automotive and aerospace components. In this technique, the molten metal is cooled into the semi-solid state before casting (H. M. Guo, 2008).

Several investigators have found that all of the above mentioned techniques have a significant effect on the microstructure of cast copper, but mechanical vibration is easier and more economical than other methods for production of castings. The mechanical vibration during the solidification of metals and alloys can modify conventional macrostructures and microstructures of as-cast alloys (M. J. LI et al, 2010). Rheocasting process is mainly use for aluminium or zinc alloy and not suitable for continuous casting of large size product.

3.5.2.5 Electromagnetic stirring

This method is also well known as an effective method for reducing the grain size but it's mainly used for copper tube product.

In this process, a coil linked with a commercial frequency electric source was installed around the mold, which consisted of a graphite inner-mold and a copper outer-jacket. During continuous casting, the melt was poured into the tundish and then tube blank was drawn continuously through the mold by means of the dummy bar, which was controlled by a motor.When a commercial frequency electromagnetic field is imposed, the solidification structure is evidently refined and grains distribute more uniformly (Xintao Li & Tingju Li. 2005).

3.5.3 Limitation of Mechanical Methods

Based on a literature review and the author's previous work experiences, although there is a reduction in the grain size and improvement of mechanical properties by using mechanical method, serious disadvantages of this technique are presented as below (Amitesh Kumar et al, 2014):

- Cost
- Long process time

- As a particular example, the frequency of vibration decides the structure of casting (the refinement of grain size increases with the increase in frequency of vibration).

3.6 Summary of this Chapter

In alloy casting, it is usually desirable for the grain structure to be fine. The major advantage of fine grain structures over cast structures is the improvement of mechanical properties and increased uniformity of properties. Grain refining methods are grouped into (a) thermal such as cooling rate control, (b) chemical by adding the nucleant agents into the melt and (c) dynamical by mechanical agitation.

Although a finer grain can be obtained by mechanical and chemical techniques, the problem of these methods is that the mechanical way is expensive. The problem of the chemical method is a lack of uniform dispersion of nucleant agents, like metal oxides, due to the ultimate problems such as difference in density between matrix and refiner, poor wettability or incompatibility between metal and oxide particles. The thermal method is known to produce metals with small grains by controlling the cooling rate.

Chapter 4 - Experimental Devices and Instruments

This section describes the experimental devices and instruments used to perform the analysis experimental data. The (a) Metallography Equipment, (b) Scanning Electron Microscope (SEM), (c) Universal Tensile Machine and (d) Spectrometer were important tools to analyse the results of the processed samples in this thesis.

4.1 Metallography Equipment

Metallographic analysis is the science of preparing a metal surface to study the metal alloy's microstructures, which usually determines the physical and mechanical properties of the metal alloy material. Metallography process prepares the specimens' surfaces to be examined by the microscope in sequential steps including; sectioning (cutting), mounting, course grinding, fine grinding, polishing, etching and microscopic examination.

Most metallographic samples need to be sectioned to the area of interest and for easier handling. Depending upon the material, the sectioning operation can be obtained by abrasive cutting (metals and metal matrix composites), diamond wafer cutting (ceramics, electronics, biomaterials, minerals), or thin sectioning with a microtome (plastics).

Proper sectioning is required to minimize damage, which may alter the microstructure and produce false metallographic characterization. Proper cutting requires the correct selection of abrasive type, bonding, and size; as well as proper cutting speed, load and coolant.

In this PhD thesis, samples for microstructural observations were cut with a clean sharp hacksaw. Sectioning of the test sample was performed carefully to avoid destroying the structure of the material.

An important factor is to describe the initial stage of grinding and, possibly the most critical factor, is the use of the right polishing cloth. Also necessary for quality examination is a proper etching procedure. Figure 4-1 shows the facility used in this research. The metallographic investigation could be used in quality control and to predict or explain the mechanical properties as the physical and mechanical properties of a metal can be related to the grain structure (Deacon, 2013).

Figure 4-1: Sample preparation kit

4.1.1 Hot Mount Press

Sectioning (cutting) is the first stage of metallography sample preparation which can be done by either a hacksaw or an automatic precision cut-off machine. After cutting the specimen, the next step is mounting. The aim of mounting specimens is for convenience in handling small sizes, difficult shapes, very soft, porous or fragile specimens during the subsequent steps of metallography grinding and polishing (Petzow, 1999). This process was conducted by using a semi-automatic hot mount press model - Struers LaboPress-1 (Figure 4-2) through the following steps:

1- Switch on power
2- Press power “up” button to bring ram to top position
3- Use “anti-stick’ on ram upper surface
4- Place specimen on ram surface
5- Press power “down” button to send ram to bottom position
6- Deposit resin into chamber

7- Use “anti-stick’ on bayonet closure surface

8- Screw bayonet closure on fully and then back a ½ turn

9- Select temperature

10- Press Heat “on” button (180ºC)

11- Press ram “up” button until pressure reach 25KN

12- Use button to maintain this pressure (2-3 minutes)

13- Wait for 5 minutes

14- Press heat “off” button

15- Turn water on and leave to cool for 3 minutes

16- Turn water off

17- Press power “down” button until pressure return to zero

18- Remove bayonet closure

19- Press power “up” button to release specimen

Figure 4-2: Hot mount press

4.1.2 Rotary Grinder

The key aim of the grinding step is to remove any damage from various sources such as: cutting, retaining non-metallic inclusions, scratching and deforming the area of interest. The final product should be free from all traces of disturbed metal. Coarse and fine grinding are the main steps in producing the smooth surface specimen suitable for microscopic examination. Coarse grinding removes heavy surface damage and fine grinding produces a flat and smooth surface.

In this thesis, all mounted samples were then ground first using coarse abrasive paper (Grade No 60) and subsequently wet and dry fine silicon carbide paper (Grit No 2500). This was all done by using the METASERV rotary pre-grinder machine (Figure 4-3).

Figure 4-3: Rotary grinder

4.1.3 Universal Polisher

Polishing is the most critical metallographic preparation step. At this step, any embedded abrasives and deformation from fine grinding and the previous damage must be completely removed. Polishing enhances the surface and makes it suitable to observe its grain structure under a microscope. In this thesis, all ground samples were then polished using diamond paste beginning with six micron and then continuing until the grinding scratches were removed (quarter micron). These were all done by using the METASERV universal polisher machine (Figure 4-4) (Zipperian, 2011).

Figure 4-4: Universal Polisher

4.1.4 Ultrasonic Cleaner

Cleaning is an important step of successful metallography sample preparation. All of remaining grinding and polishing contamination must be completely removed before etching process. In fact, all contamination remains from the previous stage, even from very fine cracks, pores of porosity or fracture samples must be completely removed. This could be done by rinsing the samples under running water and an ultrasonic cleaner machine and then wiping. Ultrasonic cleaning is the most popular and effective technique compared to rinsing, as an ultrasonic cleaner can remove all dirt using alcohol or acetone. The forward step is drying. Any remaining liquid in samples, such as cracks or porosity, must be evaporated and eliminated before the etching process. This can be done by compressed air or nitrogen gas (Petzow, 1999). Figure 4-5 (a) shows the ultrasonic cleaner and Figure 4-5 (b) shows the drying samples using nitrogen gas.

(a): Ultrasonic cleaner | (b): Drying samples using nitrogen gas

Figure 4-5: Cleaning the polished samples

4.1.5 Clean Room for the Chemical Etching Procedure

Last step of metallography sample preparation is the etching procedure. Usually the microstructure of a polished specimen will not be visible by optical microscope without an etching process due to differences in reflectivity. Etching is the process of using strong acid. This acid is usually stored at room temperature. Etching the surface of a specimen can be by wiping it with a piece of cotton wool or absorbent cloth, which has been soaked in the etchant. The surface of polished sample must be exposed to chemical attack and after that the light from an optical microscope can be reflected from the sample surface, depending on how the surface of sample is etched. For this aim, the following steps must be considered carefully (Petzow, 1999) and (Voort G. F., 1984):

1- Proper preparation of sample surface
2- Selection of the best etch composition
3- Control of etchant temperature
4- Control of etch time

In fact, safety is very important when etching. Be sure to wear the appropriate protective clothing and observe all WARNINGS on chemical manufacturers SDS (Safety Data Sheets).

A good policy on health and safety is essential for using acids as an etchant solutions such as (guidelines for the safe use of nitric, 2015) and (Voort G. V., 2015):

1- **Using the appropriate Personal Protective Equipment (P.P.E):** Technicians must wear safety clothes to perform this procedure in compliance with health and safety requirements. The technician who is performing the chemical etching, should wear: lab coat, two pairs of latex (or thick rubber) safety gloves, safety glasses and an appropriate mask depending on the volatility of the acid, as some acids like nitric acid can burn eye or skin or permanently damage the digestive tract

2- **Clean Room:** Etching procedures must be done under hood in the cleaning rooms. Figure 4-6 shows the cleaning room equipped with a hood.

3- **Clean Up:** Etching solution must be discarded after used and poured back into a glass container with a lid for recycling. The acid can't be reused if it doesn't give a proper etch or if it becomes discoloured or cloudy.

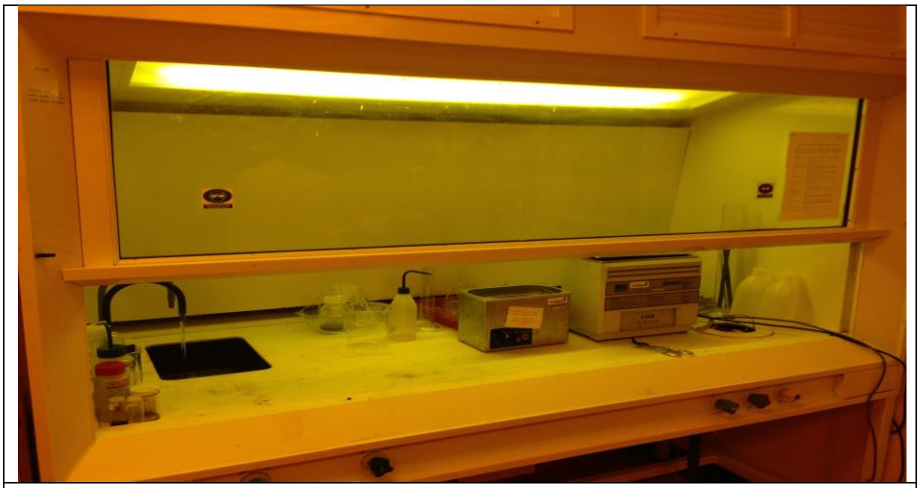


Figure 4-6: Cleaning room

The most etchant solution for copper alloys used in this PhD thesis were contained nitric acid and distilled water (50 ml, 50 ml).

4.2 Digital Microscope

Optical microscopy is used to characterize the grain structure, grain boundaries, porosity, inclusion distribution and evidence of mechanical deformation (M.R. Louthan, 1986). This process was conducted by using KEYENCE digital optical microscope which is facilitated with an image capturing facility to save the images onto a hard-drive as JPEG files. To view microstructures and oscillation marks, which are in the orders of micrometers (µm), KEYENCE digital microscope- Model VHX-1000E (Figure 4-7) was one of the most important instruments used in this thesis as an analytical tool. VH-S5 and VH-S30 were two types of microscope lens and observation system used in this digital microscope. Tabl 4-1 shows the parameters of the Keyence VHX-1000 3D profile measurement units.

Table 4-1: Parameters of VHX-1000 3D profile measurement units

Observation system model	VH-S5	VH-S30
Angle range	±80°	-60 ~ + 90
Electric stage model	VHX-S15H	VHX-S15F
Stage stroke distance	15 mm	15 mm
Resolution	0.05 µm/pulse	0.05 µm/pulse
Positioning accuracy	6 µm	6 µm
Repeatility	± 0.5 µm	± 0.5 µm
microscope lens model	VH-Z500R	VH-Z100UR
magnification	500× ~ 5000×.	100× ~ 1000×

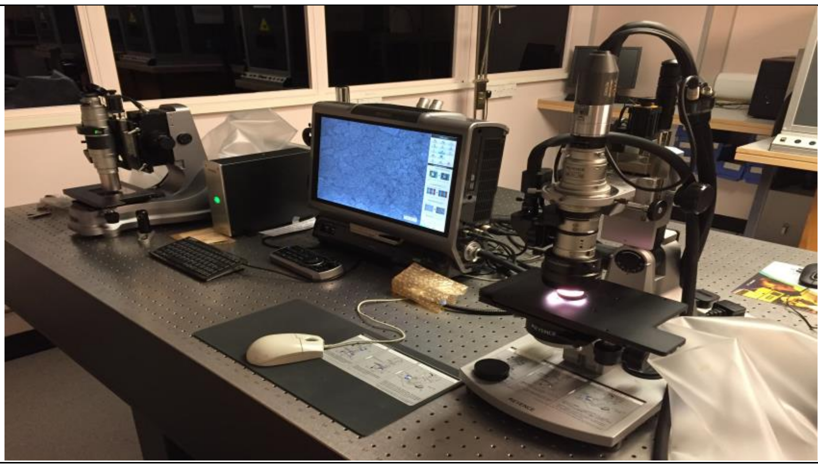


Figure 4-7: Optical microscope (Model -VHX-1000E)

4.3 SEM/EDX

Subsequent to optical microscopy, the samples were also examined using a scanning electron microscope (SEM) machine. A scanning electron microscope is a much more powerful magnification tool than any standard optical microscope which uses electrons instead of light to form an image. The first working electron microscope was built in 1933 by T Ruska. He obtained images of copper and gold surfaces at a magnification of only 10X. In the early 1960s the electron microscope was developed by Everhart and Thornley. Again, electron microscopes were further developed in 1965 and finally Cambridge Instrument Company in the U.K marketed the first commercial scanning electron microscope, and about six months later by JEOL in Japan. Since then, more and more electron microscopes have been developed and applied to material science and engineering industries.

Current SEM microscopes have certain advantages over optical microscopes. The main advantage is that SEM have a higher depth of field and greater resolution compared to OM; therefore, SEM has a higher magnification (up to 2 million times).

Apart from this, some of the new SEM machines are able to capture 3D images. On the other hand, electron microscopes have a range of limitation over the optical microscopy such as cost, elaborate sample preparation, sample size, etc. These advantages and limitations of SEM make them useful in a wide range of different applications, such as high resolution surface imaging (MCMULLAN, 1994), (Patrick Echlin, 2009) and (Michael Dunlap & J. E. Adaskaveg, 1997).

In this thesis, JEOL JSM-7400F scanning electron microscope is used to capture the high resolution images. This SEM also has Energy Dispersive X-Ray Analysis (EDX) functions which gives the elements distribution in processing. Energy dispersive X-ray fluorescence spectrometry (EDX) is a useful tool, and an easy and convenient technique to investigate the various elements (Kinoshita, 2013). Figure 4-8 , shows the JEOL JSM-7400F. EDX, is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its uses the energy of the x-rays rather than ion spark which is used for spectrometer as explained in the next section.

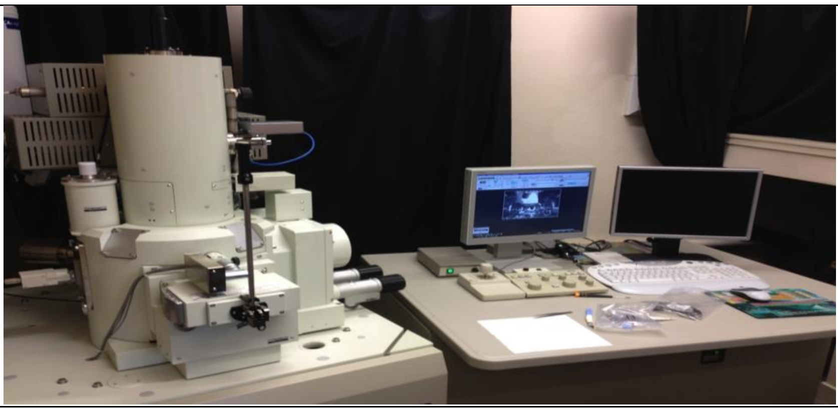


Figure 4-8: SEM/EDX machine (Model, JEOL JSM-7400F)

4.4 Spectrometer

Mass spectrometry (MS) is an analytical chemistry technique for the determination of the elemental composition of a sample. MS can identify the amount and type of chemicals present in a sample by measuring the mass-to-charge ratio of charged particles (Sparkman, 2000). In this work, mass spectrometry also used model-AMETEK - Spectromax (Figure 4-9) as an analytical technique to investigate and determine the elemental composition of cast products using following steps:

- A sample is put onto the mass spectrometer machine
- The components of the sample are ionized
- The positive ions are then accelerated by a magnetic field
- Computation of the mass-to-charge ratio of the particles
- Detection of the ions

Figure 4-9: Mass spectrometry (model- AMETEK)

4.5 Universal Tensile Machine

Tensile testing - also known as tension testing - is a destructive test (DT) process. It is probably the most fundamental type of mechanical test, which provides the following quantitative measurements:

(a) Ultimate Tensile Strength, also called UTS, is the maximum tensile stress that a material can resist while being stretched or pulled before failing or breaking. UTS can be calculated by maximum load divided by the original cross-sectional area of the test sample.

(b) Yield Strength is defined as the stress where deformation changes from being mostly elastic to mostly plastic.

(c) Ductility of a material (elongation), describes the strain at, or after, the point of fracture, and reduction of the area after the fracture of the test specimen.

The following four steps do calculation of the percent elongation;

1- Measurement of the original gauge length

2- Application of a tensile force to the material - slowly until the fracture occurs

3- Fit the broken parts back together and measure the fracture length

4- Calculate the percent elongation using the following equation:

$$\text{Percent elongation} = [\frac{\text{final gage length} - \text{original gage length}}{\text{original gage length}}] \times 100$$

The results produced in tensile tests can be used in the following aspects: (Czichos, 2004), (Czichos H. , 2006) and (Vaccari, 2002):

1- Selecting proper materials for proper applications

2- Quality control

3- Development of new materials and processes

4- To predict the behaviour of a material

In this research, this test also done to investigate and determine the quality of cast products. For this research, tensile testing was done by an Instron computer servo universal testing machine – Model 4204 (Figure 4-10 (a)) and Avery universal tensile machine – Model CCJ/DCJ120.000lb (Figure 4-10 (b)) using following steps:

1- Before starting the tensile test, a suitable grip is selected. In case of choosing the incorrect set up, the specimen may slip or even break inside the gripped area and this would lead to invalid results

2- Enter data into the computer, which is connected to the machine

3- Place the specimen into a grip

4- Ensure that the specimen is held tightly by both grips, up and down

5- Testing is allowed to run at a suitable speed

6- The force is applied until there is a fracture of specimens

The setup control selected as below (Figure 4-11):

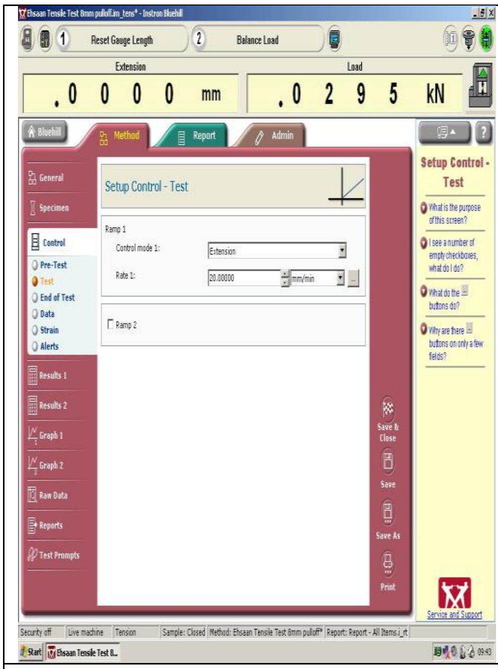
- Extension rate: 20,000 mm/min

- Shape (geometry): circular
- Gauge length of specimens: 100,00 mm
- Final length of samples: 300,00 mm

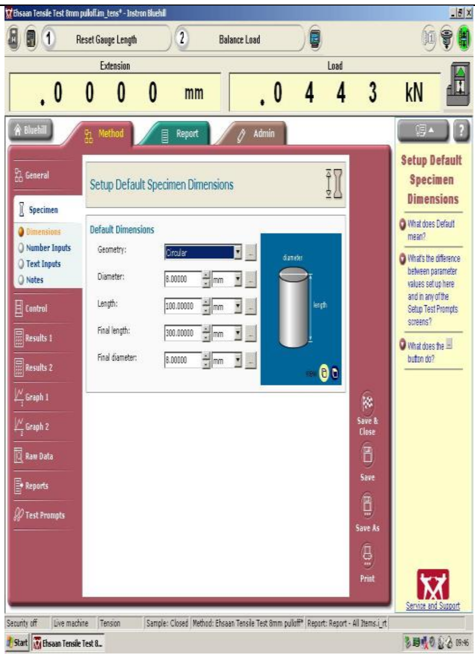
(a)Instron - Model 4204

(b)Avery - Model CCJ/DCJ120.000lb

Figure 4-10: Universal tensile machine



(a) Extension rate



(b) Dimensions

Figure 4-11: Setup control

Chapter 5 - DHP Copper Tubes

Continuous casting process enjoys certain advantages via other thermomechanical manufacturing processes, such as extrusion. Although each method has its advantages, depending on the final product and its use, the key reasons for the success of the casting process are:

a. Lower cost of capital investment and operation
b. Less scrap rate
c. Control over the process: Wide range of properties can be attained by adjusting percentage of alloying elements
d. Control over grain size: Grain size of cast component can be easily controlled by controlling cooling rate, which in turn can be used to modify the properties

Thus, if the physical and mechanical properties of continuous casting are acceptable, this method can replace other manufacturing processes. The key aim and objectives in this chapter are:

(1) To compare the physical and mechanical properties of continuous casting process and thermo-mechanical process.
(2) To investigate the influence of cooling rate control on the structure and mechanical properties of continuous cast product by changing the casting speed.

5.1 Objective 1. Comparison of Physical and Mechanical Properties of Continuous Casting Process and Thermo-mechanical Process

5.1.1 Background

The first recorded use of copper for conveying water goes back to 2750BC when it was discovered in Egypt. Currently, copper has a wide range of application in home and industry.

Historically copper tubing was expensive and only installed in prestigious buildings. But nowadays, Deoxidized High Phosphorus (DHP) copper tubes are frequently used in numerous industrial and household applications (http://yorkshirecopper.com/, 2014). The usage of copper tube has increased in many applications and industries over the decades. Currently, the usage of copper tube has grown over the last few years mostly due to its beneficial characteristics such as high corrosion resistance, high thermal-exchange efficiency, excellent erosion resistance and easy processing.

In addition to this, copper has a long useful life and is environmentally friendly - 100% recyclable, lightweight and easy to shape. These properties make copper the most cost effective material for tube application (The Copper Tube Handbook, 1995).

The main applications of copper tubes can be classified into three major categories: (a) hot or cold tap water or plumbing tubing, (b) air conditioning and refrigeration tubing (c) industrial applications such as relay or thermostat (Xintao Li et al, 2007), (M.B. Karami, 2003).

In recent years, DHP copper tubes have been gradually replaced by inner-grooved copper tube (smooth on the outside and grooved on the inside) ones to improve the efficiency of thermal-exchange for energy saving and environmental protection. Based on the statistics of the Chinese refrigeration industry union, the demand for household air conditioners was 30.5 million unit in 2005, which means that 91.6 thousand tons inner-grooved copper tubes were needed when 50 million air conditioning units were sold in only China in 2010. (Xintao Li & Tingju Li, 2005).

The traditional method of producing copper tube is by large ingot casting and extrusion but there are new methods which use continuous casting technology to cast smaller tubes. One of the proven new processes for casting smaller tubes is the planetary rolling process, which casts a much smaller hollow billet. Another new process which has just been developed is the cast-tube process which produces a continuously cast tube shell at a size suitable for drawing.

The main advantage of the continuous casting process for copper tube production is that it is an economic and flexible manufacturing process with a much smaller initial capital investment.

To ensure the acceptability of DHP copper tubes prepared by various industrial processes, the quality of the DHP copper tubes must be evaluated. In studying the properties of DHP copper tubes, it is necessary to have detailed knowledge of their mechanical properties.

Mechancial properties can be obtained by tensile test, flatenning test and tube drift expanding test (it will explained in section 5.1.3.2). To evaluate the quality and performance of the DHP copper tubes it is also necessary to have a detailed knowledge of their physical properties and the best way to do so is to examine the microstructure and metallography, and to quantify the grain size.

5.1.2 Materials for Research

Copper does not react with water but it does slowly react with atmosphere oxygen to form a layer f brown-black copper oxide. Deoxidised High Phosphorus (DHP) copper is the common alloy which is used for copper tubes and used in applications where the copper must be resistant to gassing such as production surface blisters or internal pores. The oxygen is eliminated by oxidation with phosphorus. Phosphorus is the most widley used deoxidant because of its relativity strong effect, low solubility in the solid state and relativity small effect on conductivity. It usually contains 0.015 to 0.040% phosphorus to ensure freedom from residual oxygen.

The copper charge is included; copper scrap, cathode copper and copper ingot. As shown in Figure 5-1 (a), (b) and (c), there are three methods available for producing the copper tubes, including (1) the traditional method, (2) the established method and (3) the new method. Each has its specific characteristics, as well as advantages and disadvantages. The following sections explain the various copper tube production methods and their characterizations.

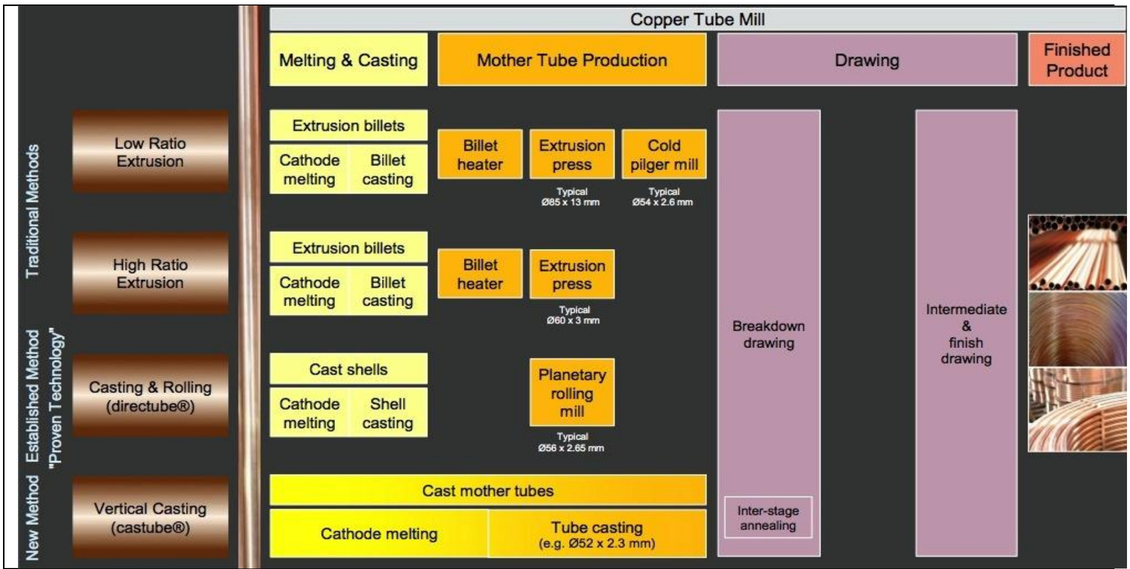


Figure 5-1 (a): Schematic of various DHP copper tubes manufacturing process (UPCAST, 2013)

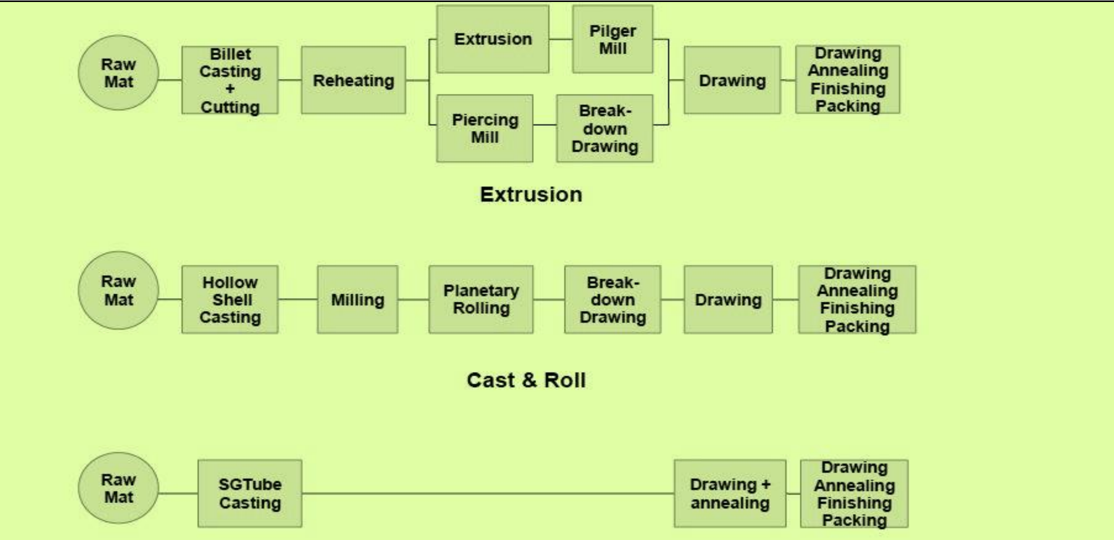


Figure 5-1 (b): Schematic of various DHP copper tubes manufacturing process adapted (UPCAST, 2013)

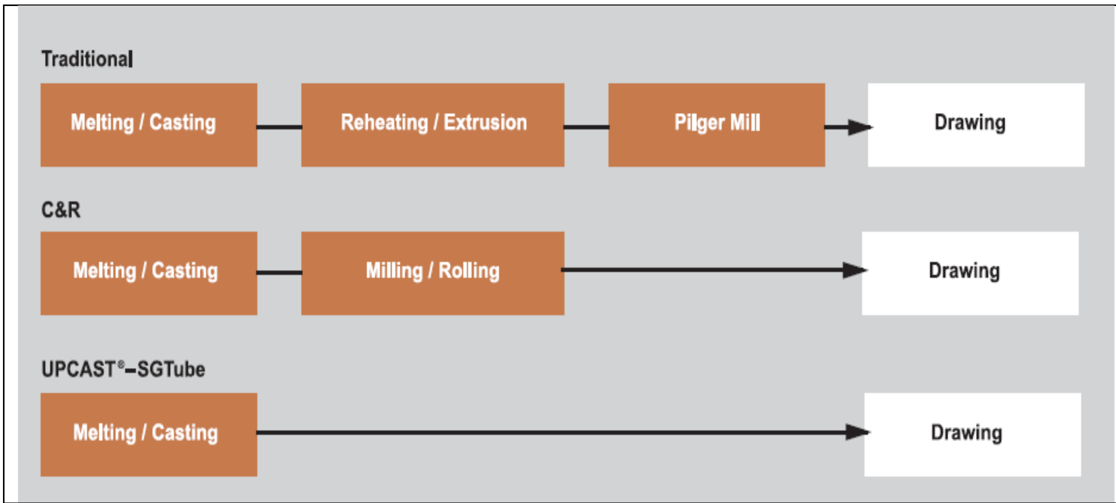


Figure 5-1 (c): Schematic of various DHP copper tubes manufacturing process UPCAST, 2013)

5.1.2.1 Traditional Method (Continuous Copper Tube Extrusion)

This method has been used for many years. In order to produce copper tubes by continuous extrusion procedure, a copper cathode is first melted and cast into a billet. The billets are then reheated using a proper hot-working temperature, and extruded into large tubes or shells. Because the shells are too large to bend, a special linear machine, known as a pilger mill, is used to draw the shells to a 'mother' tube. Pilger mill is a rolling process for metal tubes, that reduces diameter and wall thickness.

Last steps are (a) drawing, (b) annealing and (c) finishing/packaging respectively.

- Drawing simply involves pulling the hollow tube through a series of hardened steel dies to reduce its diameter.
- Annealing: drawn tubes are then passed through a continuous annealing furnace in order to improve their mechanical properties.
- Finishing/Packaging are the final steps. The tube may be cleaned to remove any traces of previous steps. As a particular example, copper cathode and copper scrap melt and cast to billet (400 kg ex) and then billet will reheat and extrude into large tube (70mm dia). Then large tube reduce to 25-40mm mother tube through the pilger mill and and finallt 25-40mm mother tube will drawn into the customer reduce size.

The key advantage of this method is continuous operation for high efficiency. However, the investment costs for a pilger mill are fairly high. Maintenance of the extrusion method is also expensive (Rainer Hergemoeller, 2009) and (Konrad, 1998).

5.1.2.2 Established Method (Planetary Rolling)

The three-roll planetary rolling mill is a special process for DHP copper tube making which consists of

- a cylindrical mandrel located inside and fixed in position by axially adjustable clamping devices
- Three uniform distributed conical rollers
- The external ring.

By the rotation of the roller, the copper tube billet is compressed and rotated around the mandrel to the forward direction.

This method requires expensive capital investment but compared to the extrusion its feature of smaller number of process steps (Bing Li, 2008) and (http://meer.sms-group.com/).

Planetary rolling is a process especially for DHP copper tube in which diameter and wall thickness are reduced in one pass by more than 90%. The principle arrangement of a planetary rolling mill comprises three rolls arranged around the outside of the tube and a cylindrical mandrel located inside and fixed in position by axially adjustable clamping devices.

The rolling process is characterised in that the three tapered rolls arranged in a planetary gearbox move transversely to the longitudinal axis in the direction of the workpiece circumference.

Figure 5-2 shows the schematic of the three-roll planetary mill.

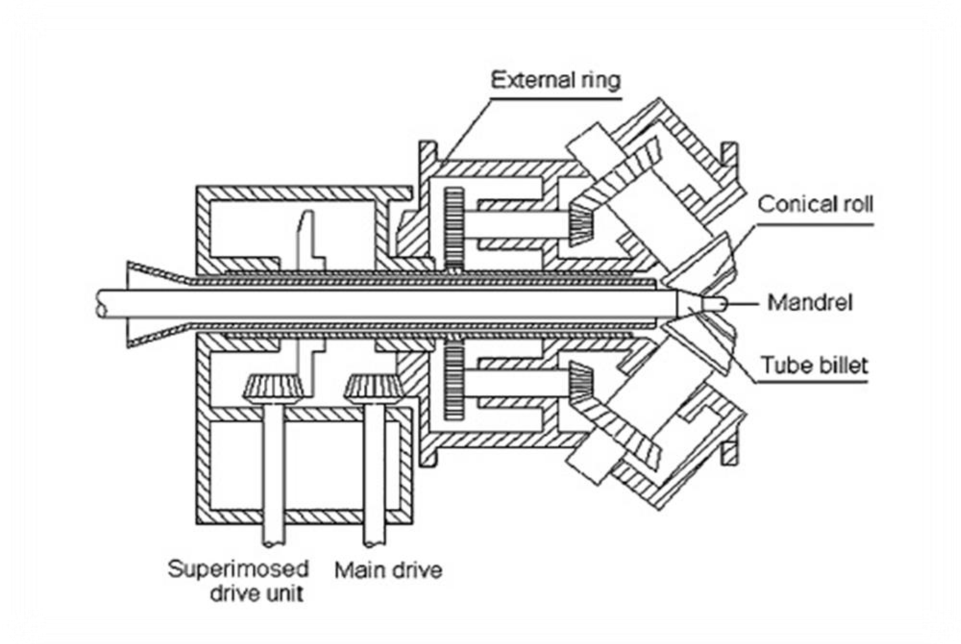


Figure 5-2: Schematic of the three-roll planetary mill (Bing Li, 2008)

Copper Rods

5.1.2.3 New Method (Continuous Casting)

The new method which consists of only melting and casting has several advantages compared to the extrusion and planetary rolling process. The key advantages include (UPCAST, 2013):

- Lower capital investment. This method is about 6-8 times cheaper than planetary rolling, which itself is already half the price of the traditional extrusion based process.
- Less operation. This method is only about 25% of a large planetary rolling unit and even much less when compared to the extrusion method.

So if the metallurgical and mechanical properties of the component produced by continuous casting are acceptable, this method can be replaced by two other methods.

The main purpose of this study was to investigate the physical and mechanical properties of the DHP copper tube samples prepared by typical industrial processes as mentioned above. The representative DHP copper tube samples analysed in this work and their corresponding processes are listed in Table 5-1.

Table 5-1: The Copper tube samples tested in this research

No	**Sample**	**Process and size (outside diameter x wall thickness)**
1	As cast	Cast at 38 x 2.3mm
2	Drawn	Cast at 38 x 2.3 mm drawn to 30 x 1.85
3	Annealed	Cast at 38 x 2.3mm drawn to 32 x 1.75 then drawn to 28 x 1.35 then batch annealed
4	Planetary rolling	Cast at about 100 x 25 mm, then rolled to 58 x 3 mm
5	Extruded 1st	Extruded to 70.45 x 3.1 mm, then drawn to 29 x 1.1 mm
6	Extruded 2nd	Extruded to 70.45 x 3.1 mm, then drawn to 24 x 1 mm

5.1.3 Experiment

The experimental procedure of this work included (a) metallography and microstructural evaluation and (b) a tube drift expanding test .

5.1.3 Metallography and Microstructural Evaluation

This section presents the first stage of experimental procedure including metallography and microstructural evaluation.

5.1.3.1.1 Metallography

By definition, metallographic analysis is the science of preparing a metal surface by grinding, polishing and etching to study the metal alloy's microstructures which usually determine the physical and mechanical properties of metal alloy materials (Deacon, 2013). In the present research, all samples were ground first using coarse abrasive paper (Grade No 60) and subsequently wet and dry fine silicon carbide paper (Grit No 2500). Then the samples were polished using diamond paste beginning with six micron and then continuing until the grinding scratches were removed (quarter micron). After polishing, the samples were cleaned by acetone in an ultrasonic cleaner and dried with nitrogen gas. Finally, the polished samples were etched using a cotton tip dipped with distilled water and nitric acid.

5.1.3.1.2 Microstructural Evaluation

There are various procedures established to evaluate the microstrucrue and measure the grain size of the etched samples. These are outlined in ASTM E112. The grain structure can be reported in one of several units (Sigworth, 2007):

1- ASTM grain size number
2- Grains per unit area
3- Average intercept distance (number of intercept divided by length)
4- Calculated average grain diameter

ASTM grain size number is the most popular unit to describe the grain size of the etched samples and in this study this unit will be used.

5.1.3.1.3 Grain Size Measurement Methods

Grain size measurement techniques are introduced for first time in 1894 by Albert Sauveur who reported the grain size in terms of the number of grains per unit area. Later, Zay Jeffries, described the approach in detail. In 1964, John Hilliard introduced the use of test circles to average out grain shape non-uniformities.

In 1974, Halle Abrams expanded this method to use three concentric circles with a total circumference of 500 mm for better statistics (Voort G. V., 2013). Now, referring to ASTM E112 (Standard Test Methods for Determining Average Grain Size), there are three methods available for grain size measurement, including;

- The comparison procedure
- The intercept procedures
- The planimetric (Jeffries) procedure.

The planimetric and intercept methods are the most useful techniques for determining the average grain size of metallic materials (ASTM Standard E112 - 12).

5.1.3.1.3.1 Comparison Procedure

The comparison method which used graded charts and tables as references is not very common in calculating grain size. In this technique, the sample photomicrographs, first taken with polarized light at proper magnification and then ASTM grain size number, will obtain by comparing of the grain structure to a series of graded images.

The comparison method is currently used in some laboratores to describe the distribution of grain size within the specimen, determination of apparent porosity in cemented carbides, inclusion rating, classification of graphite structure in cast irons. This technique may also be used if the structure of the material approaches the appearance of one of the standard comparison charts (ASTM Standard E112 - 12) and (George E. Totten et al, 2004) and (Peirson, 2005).

5.1.3.1.3.2 Liner Intercept Procedure

The intercept method is usually done through electronic software. However it can be done manually by an operator. This method involves an actual count of the number of grains intercepted and grain boundaries, per unit length of test line.

In this method horizontal and vertical lines of various lengths and separation are drawn with regards to the scale on the micrograph and in each direction the number of grains per length line is counted.

By dividing the length of the lines by the total number of grains on those lines, the average grain size can be calculated. The main limitation of this method is that in order to gain the proper results, at least five fields must be counted. The other limitation is that, the total length of the straight line drawn should cut at least 50 grains (Abrams, 1971).

5.1.3.1.3.3 Planimetric Method

Jeffries planimetric method, which defned as an actual count of number of grains within a known area, was established in 1916. This method is based on counting grains in a specified area.

This method involves an actual count of the number of grains within a known area. Jeffries planimetric method is generally performed by drawing a circle in a diameter of 50 mm^2 on the captured image. Selection of the proper magnification is very important. A magnification must be provide at least 50 grains within the measurement area.

Then grains that are located entirely inside the circle and the grains intercepting the circle must be counted separately and the average grain size calculated by using the following equation (total surface area devided by number of grains multiply surface magnification) (ASTM Standard E112 - 12) and (Jefferies Z et al, 1916) and (Engqvist. H & Uhrenius. B, 2003).

n_1 = number of grains completely inside the test circle

n_2 = number of grains intercepting the circle

$N_A = f\,[n_1 + (n_2/2)]$

f = Jeffries factor (magnification^2/circle area) = $M^2/5000$

A = Average Grain Area ($A = 1/N_A$)

The average grain size is defined by $d = (A)^{1/2}$

$G = [3.322 \text{ Log } N_A] - 2.955$

G is the ASTM grain size number

(Note that N_A is the number of grains/mm^2 at 1X)

In this technique, a count is made of the number of grains completely inside the test circle n_1 and the number of grains intercepting the circle n_2.

The total of $n_1 + n_2/2$ is multiplied by the Jeffries factor (f) for the magnification employed to obtain an estimate of the number of grains per square millimetre.

The value of (f) for any magnification can be calculated by dividing the magnification square by 5000.

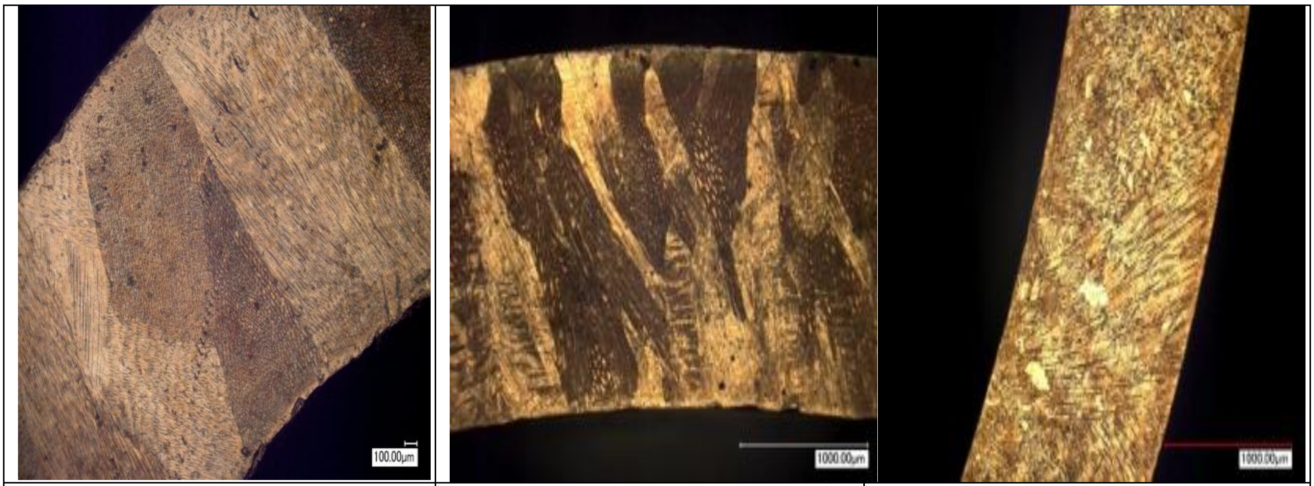
The ASTM grain size number can be calculated from the number of grains per square millimetre using the above equation.

In this research the evaluation of the grain size and microstructure of copper tubes was performed using a “KEYENCE” digital optical microscope.

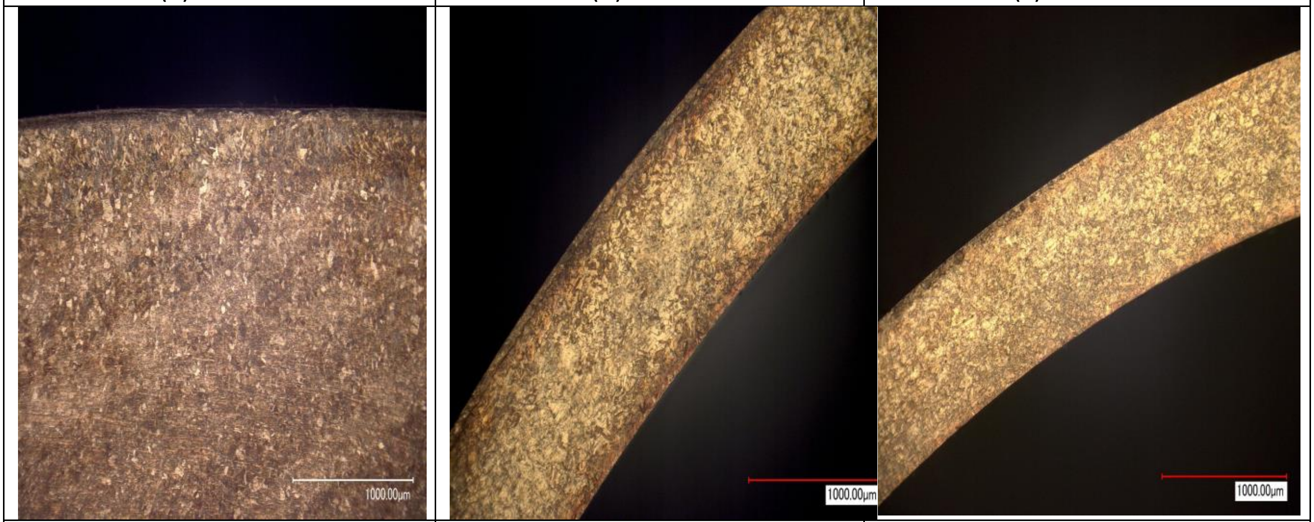
The grain size was then determined using two methods:

- The Planimetric procedure
- A new technique, which is called the “Total Grain Counting Method”.

Figure 5-3 shows the grain structure of various samples by X100.



(a) As cast | (b) Drawn | (c) Annealed



(d) Planetary rolled | (e) Extruded 1st | (f) Extruded 2nd

Figure 5-3, Grain structure of various DHP copper samples

In present work, to describe the ASTM grain size number, a proper magnification was selected which gave at least 50 grains.

A circle was drawn on the image, the grains that were located entirely inside the circle were counted and then the grains intercepting the circle were counted separately.

The average grain size was calculated by using the Jeffries planimetric equation. Figure 5-4 shows the analysis and quantification of grain size by Jeffries planimetric method

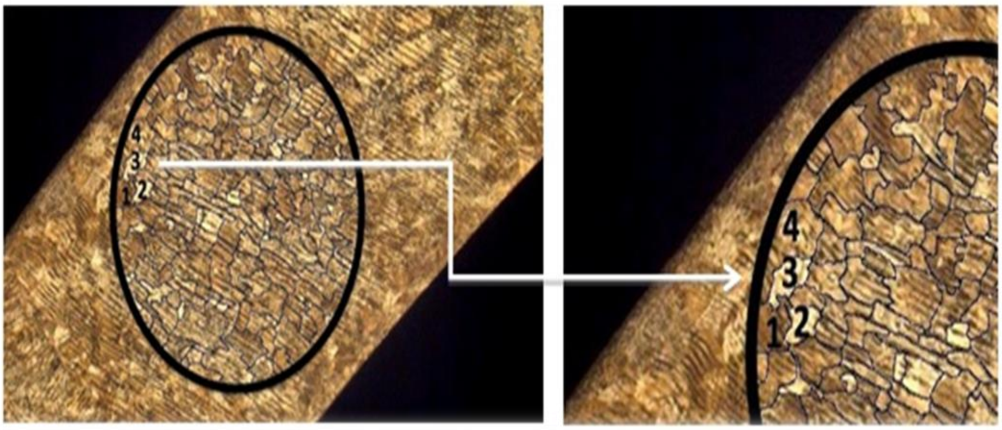


Figure 5-4: Grain size analysis by Jeffries Planimetric

The Jeffries planimetric method is not suitable for grain size measurement for large grains in thin wall copper tubes, as there are no circular areas with 50 grains or more. Thus a new method for calculating average grain size was used. To perform the total grain counting method for a tube section, first the images must be merged together and then a stitched image of the sample cross-section must be printed.

The numbers of grains were counted by hand and the total surface area of the tube cross-section was also calculated. Then the total number of grains was divided by the area of the tube cross-section to give the average grain size in millimeters squared. Figure 5-5 present the total grain counting method (using ImageJ software in order to show grain boundary contrast appears in high-magnification area).

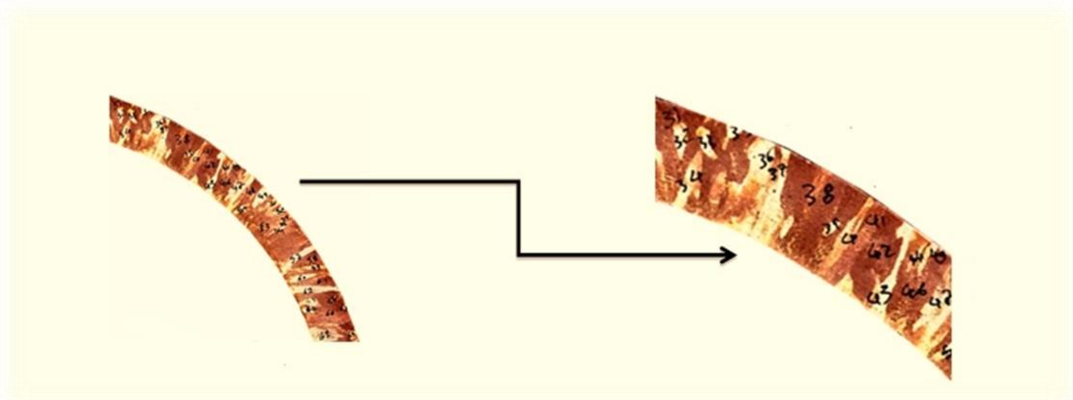


Figure 5-5: Grain size analysis by Total Grain

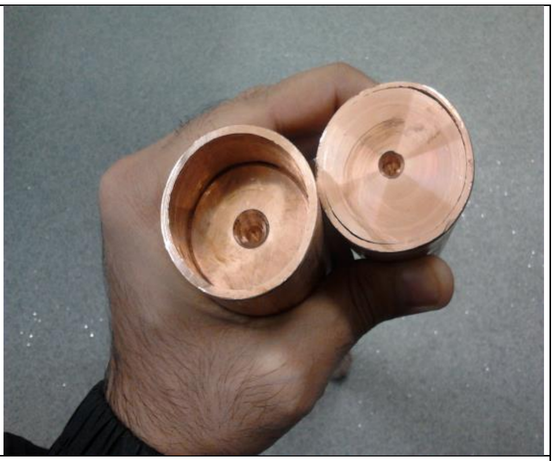
5.1.3.2 Tube Drift Expanding Test

In studying the properties of DHP copper tubes, it is necessary to have detailed knowledge of mechanical properties of the samples.

There are many different types of tests for investigation of the mechanical properties of tubes. Mechanical properties of tubes usually gain by three common testing methods involving; (a) Tensile test, (b) Tube drift and (c) Flattening test.

These mechanical tests often involve the deformation or breakage of test specimens. Each option has its own advantages and disadvantages which are explained below.

a. **Tensile Test:** Theoretically, a tensile test for a pipe is a good test because of the apparent simplicity with which it can be performed. But in reality, because pipes/tubes are circular in shape, it is difficult for tensile machines to hold/grip. The tensile test may be performed on a sufficiently long section of the entire pipe. To enable the specimen to be secured in the test machine, mandrels have to be inserted into the pipe ends, as shown in the following pictures. In this work have tried to design a special fixture to clamp the two ends. This technique has several limitations. The failure location was hard to control, since the same cross-section along the test length and the clamping may damage the pipe at those locations and weaken its strength. Also, the results were not very accurate. In our work, the clamp also moved through the pipe during the tensile test. Also, an unexpected tear on the surface of the test specimen after the tensile test was observed, as illustrated in the following Figures 5-6 and 5-7.



(a)Extra section (plug) inserted into two ends of test specimen – before tensile test

(b)Extra section (plug) inserted into two ends of test specimen – after tensile test

Figure 5-6: Tensile test of tube difficulties (moving plug)

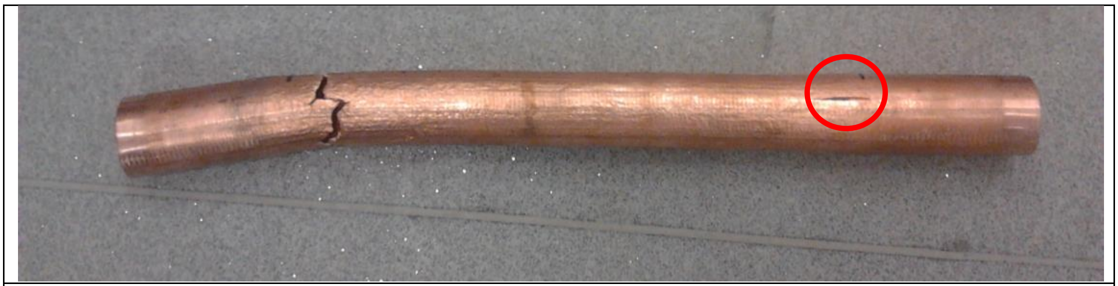


Figure 5-7: Tear on the surface of test specimen

b. **Flatening Test**: To perform this test, a section of pipe equal in length to 1.5 times the pipe diameter, but not less than 10 mm and not more than 100 mm, is flattened under a specific load using a specified load using a machine such as tensile machine. After the test, a visual inspection is used to observe the tube and to determine whether it is free from cracks and did not fracture. Observing the damage on the surface of the tube is counted as the other measurement technique. However this test is performed according to ASTM standard, but unfortunately a pass or fail is usually used to determine whether the quality of tube (damage or crack) is acceptable or not. It means, the tube will fracture upon flattening or not. In this technique we have no reliable proper value of comparison test results. The other limitation of this method is, outside diameter must no greater than 600mm. Thickness no greather than 15% of the outside diameter. Length size no less than 10mm and no more than 100 mm. This method is manily use for welded steel pipe rather than DHP copper tube.

c. **Tube Drift-Expanding Test** is expansion of the end of the test piece cut from the tube, by means of a conical mandrel, until the maximum outside diameter of the expanded tube reaches the value specified in the relevant product standard. The length of specimen is dependent on alloy materials. As a particular example, the length of the specimen for aluminium and light alloy tubes is to be not less than twice the external diameter. For copper and copper alloy tubes, the length of the specimen is to be not less than twice but not more than three times the external diameter of the tube. To perform this test, the test specimen is expanded by a mandrel until it fractures. After the test, fracture may not be visible on the surface of tube and the expanded zone of the specimen. In this research, a drift expanding test has done using a hydraulic press on controlled condition (at ambient temperature 25ºC) and with a truncated-cone shaped mandrel of hardened steel. The length of the specimen selected was less than twice the size of the external diameter of the tube. Finally, the drift expanding percentage, calculated by measuring the diameter of tube after fracture, is divided by the original diameter of tube (ASTM Standard A370 - 07b), (Tube Drift Expanding Test EN ISO 8493:1998), (Tube Flattening Test, 8492:1998), (Rules for Classification and Construction. II Materials and Welding), (Babakri, 2010). To better undestand this test, symbols, designations and units for the drift-expanding test of tubes are presented in the following Figure and Table (Figure 5-8 and Table 5-2).

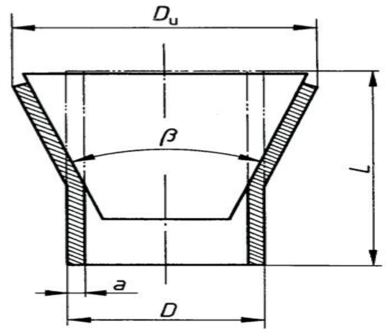


Figure 5-8: Designation of the drift-expanding test of tubes (Tube Drift Expanding Test EN ISO 8493:1998

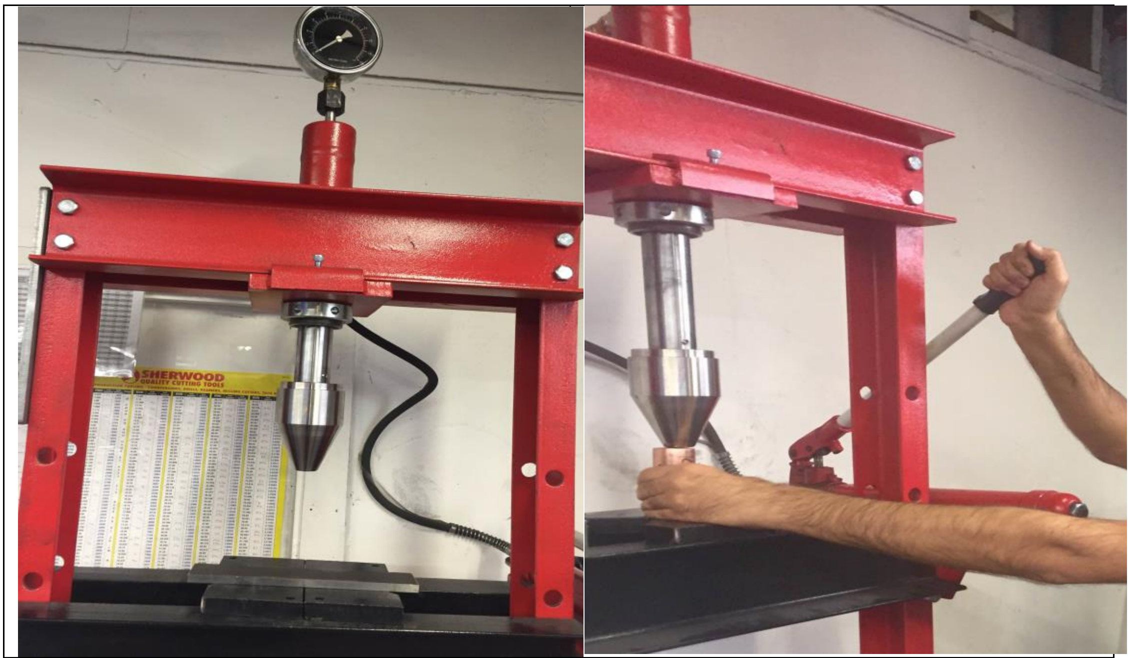
Table 5-2: Symbols, Designation and Units for the drift-expanding test of tubes, (Tube Drift Expanding Test EN ISO 8493:1998

Symbol	**Designation**	**Units**
a	Wall thickness of the tube	mm
D	Original outside diameter of the tube	mm
D_u	Maximum outside diameter after testing	mm
L	Length of the test piece before testing	mm
β	Angle of the conical mandrel	Degree

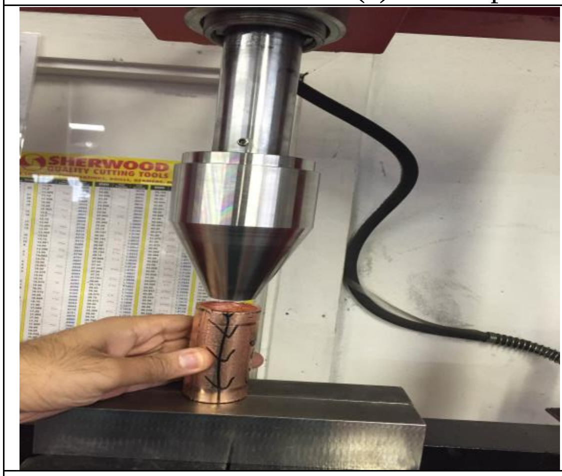
Material	**Length of specimen (L)**	**Angle (β)**
Steel	≤ 2D ≤ 1,5 D Min 50mm	30º 45º,60º Or 120º
Copper and Copper alloys	2D	45º
Aluminum Alloys	≥ 2D Min 50mm	60º

Figure 5-9 illustrates the test procedure, which has been carried out to identify the influence of the casting speed on the mechanical properties of continuous cast DHP copper tubes.

Copper Rods



(a)Drift expanding test machine



(b) Drift Expanding Test

(c) Specimen after fracture

Figure 5-9: Drift-expanding procedure

5.1.4 Results and Discussion

This section presents the results and discussion of the main finding concerning the metallography and microstructural evaluation and tube drift expanding test.

5.1.4.1 Metallography and Microstructural Evaluation

In this research, the evaluation of grain size and microstructure was determined through planimetric procedure and total grain counting methods. ASTM grain size number and grains per unit area used as a unit to describe the grain size of the etched samples prepared by typical industrial processes as mentioned above. The results of average grain sizes of copper tube samples are presented in Table 5-3.

Table 5-3: Comparison average grain size of copper tube samples

No.	Sample	Size (OD x Thickness mm)	grain size (mm2) reading 1	grain size (mm2) reading 2	grain size (mm2) reading 3	Average grain size (mm2)	The average grain per square millimeter
1	As cast	38 x 2.3	N/A	N/A	N/A	1.19	0.84
2	Drawn	30 x 1.85	0.94	0.97	1.02	0.98	1.02
3	Annealed	28 x 1.3	0.016	0.019	0.021	0.018	55.55
4	Planetary rolling	58 x 3	0.00069	0.00082	0.00092	0.0008	1250
5	Extruded 1st	29 x 1.1	0.0021	0.0027	0.0019	0.0022	454.54
6	Extruded 2nd	24 x 1	0.0016	0.0020	0.0023	0.0019	526.31

- based on the three reading, results show the variations of average grain size of different samples. The reason for this is the different manufacturing processes applied to each tube. By comparison it can be seen that the samples, which have been planetary rolled, have a smaller grain size than cast or extruded tube samples.
- The average grain size of planetary rolled sample is smallest. During the planetary rolling process, mechanical working greatly deforms the material. This deformation generates lots of energy which heats the material hot enough for full recrystallization of the grains to occur. That is why tubes produced by the planetary rolling process have very fine grains.
- It was also observed that the average grain size of the annealed samples was smaller than cast tube samples. The reason for this is because during the annealing process, the cast samples were heated to the recrystallization temperature, which was about half the melting point. In the new structure

dislocation density has reduced and eliminated. So the grains within the structure recrystalize into many fine grains.

- Extrusion is a highly mechanical deforming process that can alter the grain size, and orientation can substantially reduce the grain. So after the first extrusion, the grains become smaller.

5.1.4.2 Tube Drift Expanding Test

The mechanical properties of the DHP copper tube samples were prepared by various industrial processes and were investigated using the tube drift expanding test. The calculated data and the drift expanding test results are illustrated in Figure 5-10 and Table 5-4.

Table 5-4: Drift expanding results

No.	Sample	Size (OD x Thickness mm)	Expanding Percentage (%) reading 1	Expanding Percentage (%) reading 2	Expanding Percentage (%) reading 3	Average Expanding Percentage (%)
1	As cast	38 x 2.3	27	29	31	29
2	Drawn	30 x 1.85	30	31	33	31
3	Annealed	28 x 1.3	40	37	38	38
4	Planetary rolling	58 x 3	50	53	52	51
5	Extruded 1st	29 x 1.1	44	46	43	44
6	Extruded 2nd	24 x 1	48	47	44	46

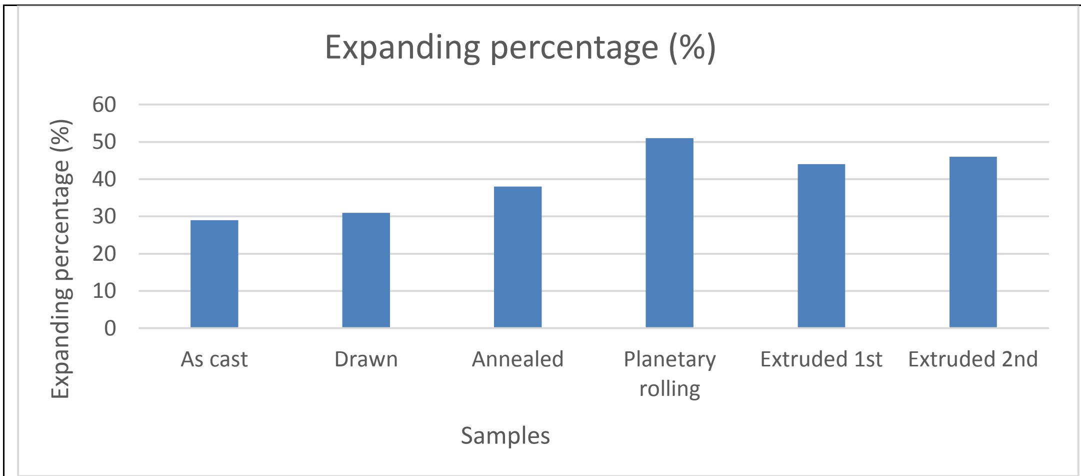


Figure 5-10: Comparison average expanding percentage of copper tube samples

The Hall-Patch relation describes the influence of grain size on the mechanical properties of alloys. Smaller grains generally improve the formability of a material. Ductility of material is defined as an ability of material to plastically deform, which involves dislocations. Smaller grain sizes equals a greater grain boundary area unit volume. Grain boundaries stop dislocations.

Thus, an easy way to improve the strength of a material is to make the grains as small as possible. Experimental results confirmed smaller grains have better expanding percentage. Copper tubes produced by planetary rolling have the smallest grain size and better expanding percentage compared to other processes. During three-roll planetary rolling, the microstructure of copper tube with initial columnar grains develops into an equiaxed grain structure due to the large rolling deformation and high rolling temperature.

Most metal manufacturers will attempt to keep grain size to a minimum, but in tube production process, casting has the largest grain size and the lowest expanding percentage.

The next chapter will focus on explaining a new way to reduce the grain size of tubes without changing process, and without adding any grain refiner.

5.1.5 Conclusion

Metallography analysis has been carried out on various copper tube samples, comparing casting, drawing, annealing, planetary rolling and extrusion. From the above results, it can be concluded that:

1. There is a significant correlation between average grain size and expanding percentage. The smallest grain size has the highest value of expanding

percentage and the largest grain size has the lowest value of expanding percentage.

2. The average grain size for different tubes may vary, depending on the manufacturing process. Planetary rolling has a smaller grain size than cast or extruded tube samples.
3. The average expanding percentage for different tubes may also vary, depending on the manufacturing process. Planetary rolling has a better expanding percentage than cast or extruded tube samples.
4. One of the methods to measure the average grain size is to use the Jeffries planimetric method, but it is not sufficient for all tube samples. The new standardized methods to measure the average grain size can be used if the samples have large grains.
5. During the three-roll planetary rolling, the microstructure of copper tube with initial columnar grains developes into an equiaxed grain structure due to the large rolling deformation and high rolling temperature.
6. The microstructure of copper tube significanty influences formability and properties due to the three planetary rolling process.

5.2 Objective 2. Influence of Casting Speed on the Structure and Mechanical Properties of a Continuous Cast Product

This section looks at the influence of the thermal method grain refinement which is known to produce metals with small grains by controlling the cooling rate. This chapter will provide a description of the efficiency of casting speed on the microstructure and drift expanding of continuous cast DHP copper tubes.

5.2.1 Background

The previous objective showed, tubes which have been cast with the continuous casting have the larger grain and lower expanding percentage compared to other industrial processes. However, the grain size in the cast structure was too big for further drawing but developed a new withdrawal system by controlling the solidification cooling rate and increasing the casting speed, which will be explained in this section. This will enable the system to cast tube with much smaller grain size and better expanding percentage.

5.2.2 Introduction

Due to the requirement of good quality production, an excellent global factor is needed for the purpose of obtaining high mechanical properties. A mechanical property has a correlation with grain size. High mechanical properties are achieved with a small grain structure. As explained in the chapter literature review, there are three ways in which grain size can be altered: by (a) thermal means, (b) chemical means and (c) by mechanical means.

This section looks at the first case, thermal means, which has very substantial cost benefits over the other two types of grain refinement in that it does not require large pieces of equipment that vibrate or mix and does not use any exotic metals as feed stock.

Instead, what thermal methods require, is a change in parameters like casting speed, liquid melt temperature or cooling water rate. In this work, characterization of the influence of casting speed on the structure and mechanical properties of continuous cast DHP copper tube has been carried out by a drift expanding test and grain size reading.

5.2.3 Materials for Research

In order to understand the efficiency of casting speed, further study has been done. Four casting speeds have been studied in this research, including 1040 (mm/min), 1140 (mm/min), 1220 (mm/min) and 1360 (mm/min) respectively. Physical properties are obtained by metallography procudeure.

Then, mechanical properties of continuous cast DHP copper tubes have been investigated by a drift expanding test. Table 5-5 presents the copper tube samples tested in this study.

Table 5-6: The copper tube samples tested in this research

Sample	OD (mm)	Thickness (mm)	Pull Dist. (mm)	Accl. (Sec)	Decl. (Sec)	Water Flow Rate (ltrs/min)	Casting Speed (mm/min)	Product (Kg/hr)
Cast 1	38	2.3	3	0.005	0.005	60	1040	144
Cast 2	38	2.3	3	0.005	0.005	60	1140	158
Cast 3	38	2.3	3	0.005	0.005	60	1220	169
Cast 4	38	2.3	3	0.005	0.005	60	1360	189

5.2.4 Experiment

The experimental procedure of this section was include:

(a) metallography and microstructural reading

(b) tube drift expanding test.

5.2.4.1 Metallography

Samples for microstructural observations were cut with a clean sharp hacksaw. Sectioning of the test sample was performed carefully to avoid destroying the structure of the material. After the sample was sectioned to a convenient size, samples were then ground by using coarse abrasive paper (grade number 60) and subsequently wet and dry fine silicon carbide paper (grit number 2500) SiC papers and polished on a cloth with a diamond suspension and lubricating solution. The grinding and polishing were both carried out on a ‘Struers machine’. After polishing, the samples were cleaned by acetone in an ultrasonic cleaner and dried with nitrogen gas. For etching, nitric acid and distilled water were used.

5.2.4.2 Tube Drift Expanding Test

Same as objective one, the drift expanding test was done in order to measure the mechanical properties of copper tubes. This was done by a hydraulic press and mandrel. The length of the specimen selected was less than twice the size of the external diameter of the tube (as a particular examples, 19mm length ooof the specimen was selected to 38mm outside diameter tube). Finally, the drift expanding percentage, calculated by measuring the diameter of tube after fracture, was divided by the original diameter of tube.

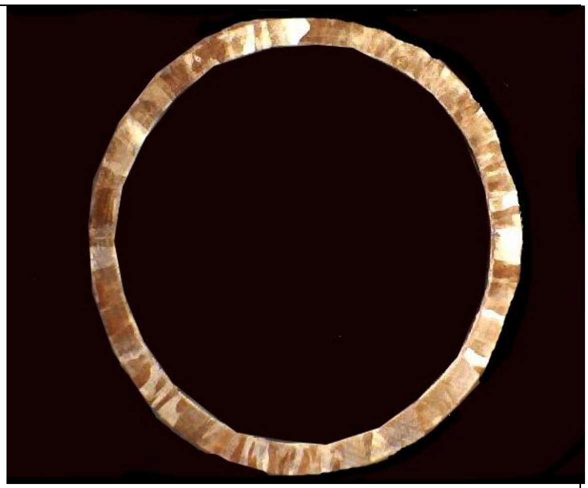
5.2.5 Results

The results is divided to two major sections. The first section described the analysis data for metallography and the second section further analysis for tube drift expanding test respectively.

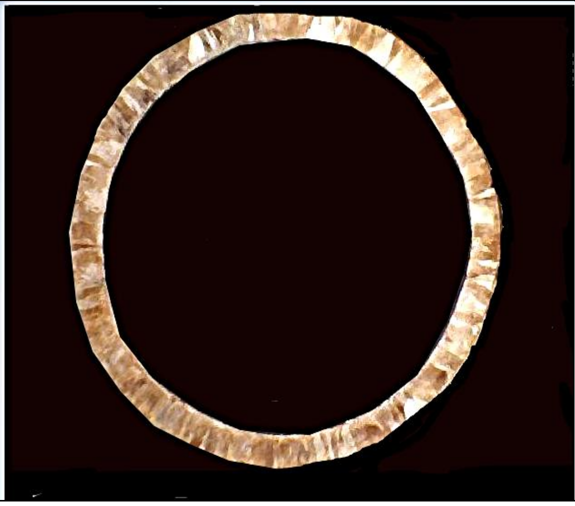
5.2.5.1 Metallography

The effect of casting speed on the structure of the continuous cast DHP copper tube is illustrated in Figure 5-11. It must be noticed that fine grains can be achieved by increasing the casting speed, as seen in sample 1, 2, 3 and 4 in this figure.

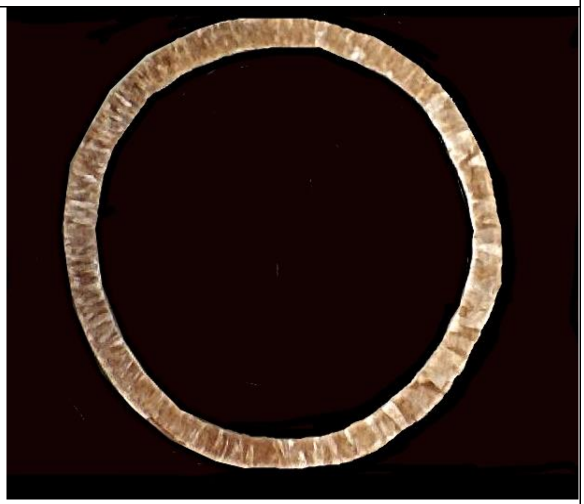
Cast 1



Cast 2



Cast 3



Cast 4

Figure 5-11: Comparison grain structure of copper tube samples

5.2.5.2 Tube Drift Expanding Test

The results of the average expanding percentage of copper tube samples are presented in Figure 5-12. Table 5-6 shows the average expanding percentage of the continuous cast DHP copper tube samples, which are explained on Table 5-5. It can be seen that the cast number four samples have a higher drift expanding percentage (improved by 29 % to 36 %).

Table 5-6: Drift expanding results

Sample	Test 1	Test 2	Test 3	Speed (mm/min)	Average Expanding Percentage (%)
Cast 1	31 %	28 %	27 %	1040	29 %
Cast 2	30 %	32 %	28 %	1140	30 %
Cast 3	32 %	31 %	33 %	1220	32 %
Cast 4	38 %	35 %	36 %	1360	36 %

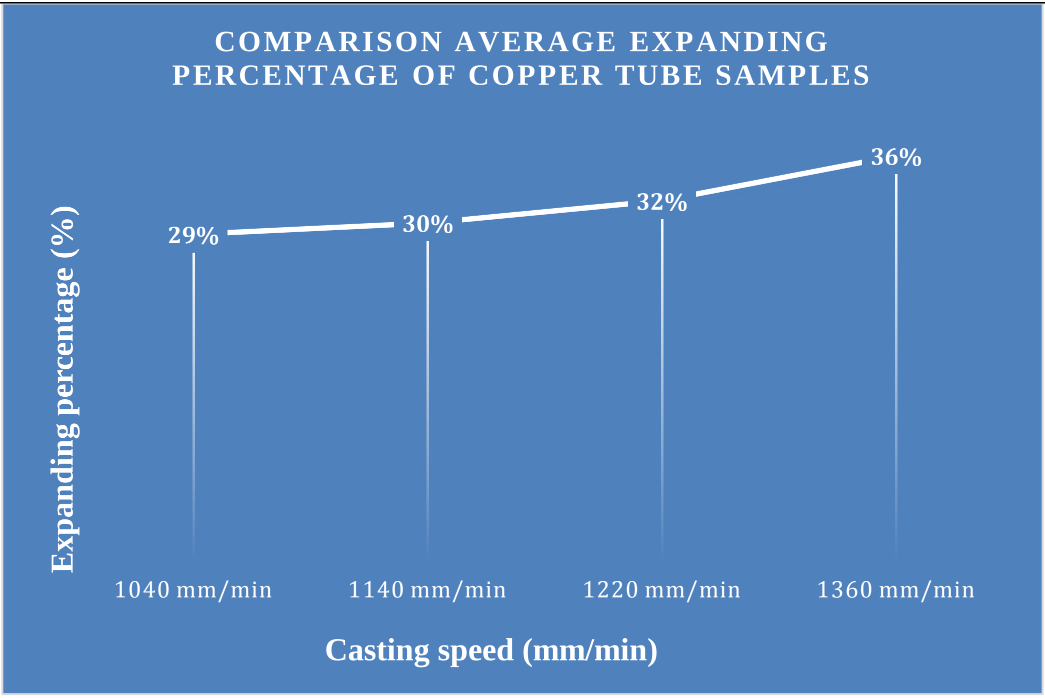


Figure 5-12: Comparison of average expanding percentage of copper tube samples

The previous section showed that the average expanding percentage of as cast DHP copper tube raised from 29% to 38% by further drawing and annealing steps.This section concludes that by increasing the casting speed from 1040 mm/min to 1360 mm/min, the average expanding percentage raised from 29% to 36% which was a significant achievement. This is a significant difference taking into account the change of only casting speed with no difference in the chemical composition of the material as well as the general method of production.

5.2.6 Discussion

It was observed that, the cooling rate has a very significant effect on the grain size of tubes. This observation is defined with following phenomena (Dahotre, 1998), (Jingchen, 2015), (L.A. Dobrzañski, 2007), (Zhiliang NING, 2007), (Pryds, 2000) :

1- Faster cooling results in large values of growth velocity which result in an increase in the number of effective nucleants and a finer grain size.
2- Faster cooling results in an increased degree of constititutional and the amount of undercooling which result in fine grain structure.
3- Faster cooling results in an increase of the amount of grain boundaries. It is known from the above observation on the metallography analysis of grains, that the number of columnar grains increases after grain refining by increasing the casting speed. As is well known, smaller grains have greater ratios of surface area to volume, which means a bigger ratio of grain boundaries to dislocations. The more grain boundaries that occur, the higher the strength.
4- Increasing casting speed leads to a change in the heat conduction and solidification condition, which results in making it possible to obtain a structure with finer grains. This is based on a thermal change because the higher the casting speed gets, the faster the material goes from liquid to solid.

5.2.7 Conclusion

From the above experiment results, some important conclusions can be drawn. Following conclusions are derived from the experimental results:

1- Tubes can be produced with a smaller grain without any changing in the process and without adding any nuclient agent. This new technology may become the next stage in tube production.

2- Once the speed is increased from 1040 mm/min to 1360 mm/min, the end result produces an increase in the production rate from 144kg/hr to 189kg/hr.

3- When casting speed was increased from 1040 mm/min to 1360 mm/min, significant improvements of mechanical and physical properties were observed. With the increasing of the casting speed, the drift expanding percentage increased, and the grain structure tended to become finer in structure.

4- An economical process has been studied to produce continuous cast DHP copper tube fine grain structure by increasing the casting speed. A significant achievement of the fine grain process is to produce a uniform structure and enable a greater reliance to be placed on the manufacturing process.

5- One limitation observed in this study is that once the casting speed is increased above the 1360 mm/min by even a minute, it would result in a casting fracture. Thus, at a high casting speed, casting speed changing should be avoided or slower speed changing rate in continuous casting should be used.

Chapter 6 - Copper Rods

Effect of Various Casting Parameters on the Mechanical Properties of Continuous Cast Copper Rod

This section looks at the influence of various solidification parameters on tensile strength, elongation percentage and microstructure of various continuous cast copper alloys. The process was investigated on 7 copper alloys included;

- CuZr
- CuSnP
- OFCu
- CuSn
- Aluminum Bronze
- CuAg
- CuMg

The reason for selecting the various copper alloys was due to the various industrial trial done at Rautomead.

6.1 Background

The previous chapter concludes that the mechanical properties of continuous casting are lower than thermomechanical methods. Apart from this, (a) alloying elements and (b) grain refinement techniques, by controlling the cooling rate, both are accepted as successful methods of increasing the mechanical properties of continuous cast product by refining the grain structure.

The key aims and objectives in this chapter are to investigate and determine how the various solidification parameters affect the tensile strength and elongation percentage of continuous cast products. The purpose of experimental studies in this chapter are to determine the influence of changes in solidification parameter conditions in the process of constant casting of various copper, using the Rautomead continuous casting machine including:

(a) alloying elements

(b) water flow rate

(c) casting speed

(d) pull distance

(e) melt temperature

(f) cleanout cycle

(g) casting direction

(h) supercooler size

6.2 Materials for Research

Copper cathode is used as the raw material input to produce copper rod in 8-22 mm diameter. The copper cathode feedstocks were melted in a Rautomead RS (commercial name) continuous casting machine. Mass spectrometry was used (model: AMETEK) as an analytical technique to determine the chemical composition of metallic samples.

6.3 Experiment

The experimental procedure of this section was working on the impact of various parameters on the microstructure, tensile strength and elongation percentage of copper alloys fabricated by continuous casting technology. These parameters were: (1) water flow rate, (2) casting speed, (3) alloying element, (4) pull distance, (5) melt temperature, (6) cleanout cycle, (7) continuous casting direction and (8) super-cooler size.

6.3.1 Alloying Elements

It has been previously reported that the amount of alloying elements play a significant role in determining the properties of casting alloys (Muramatsu, 2012).

Although the relationship between the ultimate tensile strength (UTS) and the electrical conductivity (EC) for the drawn CuZr binary alloy wires and other conventional copper alloys have been reported, the effect of increasing zirconium content on the mechanical properties of continuous cast copper alloys has not been investigated previously. In this thesis, the effect of zirconium on the mechanical properties of continuous cast copper alloy are investigated.

Ideally, copper alloys used in miniaturized electronic devices should exhibit a combination of high strength and high electrical conductivity. NGK Japan (Rautomead;s customer) have previously reported on: (i) the fine dendrite microstructure of hypoeutectic Cu-x at% Zr (x = 0.5–5) alloys created by copper mold casting, (ii) the change in this microstructure with heavy wire-drawing to a lamellar structure of nanometer-scale layers of copper and a Cu/Cu-Zr intermetallic eutectic phase, and (iii) the good balance between strength and electrical conductivity that these drawn-wires exhibit. Despite this, the mold sizes available for copper mold casting greatly limit the potential for rapid solidification, thus making copper mold casting unsuitable for mass production.

The focus in this study is therefore on applying a vertical upwards continuous casting mass-production method for manufacturing of Cu-Zr alloy rods (range of Zr% from 2.6 to 6.8%). The microstructure and mechanical characteristics of these vertical upwards continuous casting rods were investigated.

Experimental work to produce 15 mm diameter CuZr rod were performed to evaluate the effect of alloying elements on the mechanical properties of CuZr alloys. In this study, several small batches of samples were cast using different alloy contents.

Cu-Zr alloy rods were produced at Rautomead Ltd. For this, feedstock specimens were first prepared from 8mm diameter oxygen free copper (OFC) wires and 13 mm diameter Cu-50 mass% Zr cored-wires purchased from Affival.

The preparation of this feedstock was controlled by varying the intermittent-injection speed of each component to given an alloy composition of Cu-x at% Zr (x = 2.6, 2.8, 3.45 and 6.8), after which it was melted in a 500 kg capacity graphite crucible at a constant temperature of 1300 °C.

Oxidation of the molten metal surface was suppressed by using a graphite flake cover and a flow of argon gas. Using a water-cooled mold made from a cylindrical graphite die wrapped in copper tube, continuous casting was performed by pulling vertically upward. Graphite dies with inner diameters of 12 mm were prepared. The cast rod was pulled up by servo-controlled pinch rollers with an intermittent cycle; the average upwards-casting speed being 1400 mm/min.

In order to investigate the alloying effect of Zr on the mechanical properties of CuZr alloy, a tensile test at room temperature was carried out according to ASTM standard. Alloy contents are summarised in Table 6-1. Three samples are selected and an average taken and then from the generated data the ultimate tensile strength and percentage elongation of each sample were calculated.

Copper Rods

Table 6-1: CuZr samples tested in this research

Sample	Rod dia. (mm)	Die	Pull Dist. (mm)	Pull Dwell (Sec)	Accl. (Sec)	Decl. (Sec)	Water Flow Rate (ltrs/min)	Casting Speed (mm/min)	Zr (%)
Cast 1	12	Graphite	9	0.5	0.2	0.2	45	1400	2.67
Cast 2	12	Graphite	9	0.5	0.2	0.2	45	1400	2.80
Cast 3	12	Graphite	9	0.5	0.2	0.2	45	1400	3.45
Cast 4	12	Graphite	9	0.5	0.2	0.2	45	1400	6.80

6.3.2 Water Flow Rate

The aim of this section was to understand the efficiency of water flow rate and tensile strength and elongation percentage of continuous cast copper alloy. The trial produced a vertically upward cast 8mm diameter CuSnP sample. Phosphor bronze (CuSnP) is an important alloy of copper with 0.5–11% of tin and 0.01-0.35% phosphorus. The tin increases the corrosion resistance and strength of the alloy. The phosphorus increases the wear resistance and stiffness of the alloy. Add phosphorus to CuSn reduce the viscosity of the molten alloy, which make it easier and cleaner to cast and reduce grain boundaries between crystals. Phosphor bronze is used for various industrial application such as bolt. It is also use for various other application where resistance to fatigue, wear, and chemical corrosion are required such as electrical applications. Rautomead's customer required this alloy for MIG (metal inert gas), TIG (Tungsten Arc Welding) as a welding wire (0.8mm, 1mm, 1.2mm, 1.6, 2.4mm dia). Springs in electrical application due to the good conductivity and corrosion resitance was the other application of this alloy.

The alloy was Sn 0.65% and P 0.03% balance Cu. In this investigation, several small batches of samples were cast at different water flow rate conditions.

Different water flow rates have been studied in this research and then tensile strength and elongation percentage of continuous cast was investigated by a universal tensile machine. Three samples were selected and an average taken. Table 6-2 gives the copper samples tested in this study.

Table 6-2: CuSnP samples tested in this research

Sample	Rod dia. (mm)	Die	Pull Dist. (mm)	Pull Dwell (Sec)	Accl. (Sec)	Decl. (Sec)	Casting Speed (mm/min)	Water Flow Rate (ltrs/min)
Cast 1	8	Graphite	10	0	0.02	0.02	3500	45
Cast 2	8	Graphite	10	0	0.02	0.02	3500	40
Cast 3	8	Graphite	10	0	0.02	0.02	3500	30
Cast 4	8	Graphite	10	0	0.02	0.02	3500	20
Cast 5	8	Graphite	10	0	0.02	0.02	3500	15

6.3.3 Casting Speed

Previous research shows that, the casting speed is one of the major controlling parameters of the metallurgical quality of the cast product (Sadler, 2013). The aim of this section was also to observe the relationships between casting speed and mechanical properties of continuous cast copper alloys.

Low and high casting speed coils of OFCu continuous cast copper alloys were produced and then the elongation percentage and tensile strength was calculated on all investigated specimens. OFCu ws selected due to wide industrial applications such as enamelled wire, data communication wire, telephone wire and super fine wire. The representative copper samples analyzed in this research are listed in Table 6-3.

Table 6-3: OFCu samples tested in this research

Sample	Rod dia. (mm)	Die	Pull Dist. (mm)	Pull Dwell (Sec)	Accl. (Sec)	Decl. (Sec)	Water Flow Rate (ltrs/min)	Casting Speed (mm/min)
Cast 1	8	Graphite	0.5	0.2	0.005	0.005	45	2500
Cast 2	8	Graphite	0.5	0.2	0.005	0.005	45	4500
Cast 3	8	Graphite	0.5	0.2	0.005	0.005	45	6000
Cast 4	8	Graphite	0.5	0.2	0.005	0.005	45	7800

6.3.4 Pull Distance

In continuous casting process, the distance of one pull in one cycle for withdrawing the cast is called pull distance. Push/pull is in the direction to the withdrawal direction of casting. Push/pull in withdrawal is in order to prevent cracks from occurring on the surface portion of the solidified shell of the cast strand along with shrinkage of the solidified shell of cast strand.

One of the purposes of this research was to experimentally investigate the dependency of the pull distance and mechanical properties of continuous cast copper alloys.

The cast trial was attempted using a standard Rautomead upward continuous casting machine setup for 8 mm rod, which consisted of a varying pull distance. The alloy was 0.3 % Sn balance Cu.

Low tin copper is an alternative conductor material for low current and signal cable, telecommunication. Rautomead;s customer required this alloy for automotive connector application. For the mentioned application, low tin copper can be replaced by Cu-ETP copper rods while CuETP is the most common copper. It is universal for electrical applications. CuETP has a minimum conductivity rating of 100% IACS and is required to be 99.9% pure. It has 0.02% to 0.04% oxygen content (typical). Most ETP sold today will meet or exceed the 101% IACS specification. Low tin copper have better mechanical strength when both CuSn and CU ETP have the same density (8.92 g/cm^3).

The tensile test of the 8mm dia Cu0.3%Sn cast alloys was conducted at room temperature using a universal tensile testing machine with a gauge length of 100mm and cross-head speed of 10 mm/min. For each test, tensile strength and percent elongation was calculated using Hooke's law. The representative Cu0.3%Sn copper samples analyzed in this work are listed in Table 6-4.

Copper Rods

Table 6-4: CuSn samples tested in this research

Sample	Rod Dia. (mm)	Die	Pull Dwell (Sec)	Accl. (Sec)	Decl. (Sec)	Water Flow Rate (ltrs/min)	Casting Speed (mm/min)	Pull Distance (mm)	Product (Kg/hr)
Cast 1	8	Graphite	0.015	0.010	0.010	55	970	3	26
Cast 2	8	Graphite	0.015	0.010	0.010	55	1700	4	46
Cast 3	8	Graphite	0.015	0.010	0.010	55	2100	5	57
Cast 4	8	Graphite	0.015	0.010	0.010	55	2700	6	73

6.3.5 Melt Temperature

Melt superheating treatment is an effective method of grain refinement (Sengupta, 2005). In the past decades, the effects of melt superheating on aluminium and magnesium alloy have been studied (Chen, 2013) and (JIE Wan-qi, 2003).

In the present research, an experimental investigation on continuous casting of Oxygen Free Copper (OFCu) has been conducted. The aim of this work was to determine the optimum point at which the casting temperature parameter produce good quality casting and the influence of casting temperature in the range of 1140°C to 1097°C on the tensile strength and elongation percentage in continuous cast oxygen free copper (OFCu) from high-purity copper cathode (LME grade A) to obtain the optimum treatment temperature.

The trials were carried out on the model RS080 vertically upwards-continuous casting machine. Pouring was done with four different temperatures at 1140°C, 1120°C, 1100°C and 1097°C. For all samples, a standard Rautomead set-up for 8 mm rod was utilised, which consisted of an overall speed of 4.3 m/min (71.67 mm/sec). Then the tensile strength and elongation percentage of continuous casting was investigated by the universal tensile machine. Three samples are selected and an average taken. Table 6-5 gives the copper samples tested in this study.

Copper Rods

Table 6-5: OFCu samples tested in this research

Sample	Rod dia. (mm)	Die	Pull Dist. (mm)	Pull Dwell (Sec)	Accl. (Sec)	Decl. (Sec)	Casting Speed (mm/min)	Water Flow Rate (ltrs/min)	Melt Temperature (°C)
Cast 1	8	Graphite	0.5	0	0.002	0.002	4300	45	1097 (°C)
Cast 2	8	Graphite	0.5	0	0.002	0.002	4300	45	1100 (°C)
Cast 3	8	Graphite	0.5	0	0.002	0.002	4300	45	1120 (°C)
Cast 4	8	Graphite	0.5	0	0.002	0.002	4300	45	1140 (°C)

6.3.6 Cleanout Cycle

The aim of this section was to understand the relationships between the cleanout cycle and the mechanical properties of continuous cast copper alloy. The cleanout cycle is define a facility, which can be used when casting specific copper alloys, for example aluminum bronze to remove oxidized layer film through a cycle.

The way the cleanout cycle works is that after the rod has been casting at the run speed for a specified run time, the speed then ramps down over a specified ramp down time to a specified cleanout speed.

The output of the rod then remains at this lower cleanout speed for a specified cleanout time before it starts ramping back up again over a specified ramp up time back to the original run speed. It will then remain at the run speed until the run time has elapsed again making the cleanout cycle start again. Figure 6-1 shows the cleanout cycle graph. For the cleanout cycle to work, the cleanout speed is normally lower than the run speed. The run time, ramp down time, cleanout speed and time and ramp up time are all values, which can be selected and altered on the machine control touch screens. Setting the run time value to zero will turn the cleanout cycle off. Changes to the cleanout operating values on the touch screen whilst casting, should only be done by an experienced operator and may result in rod breakages or defects (http://www.rautomead.co.uk).

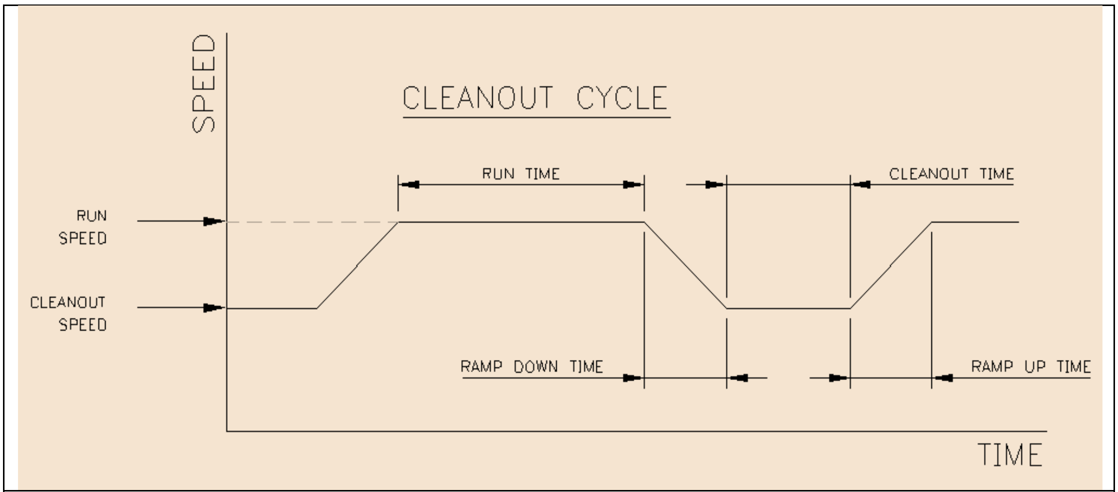


Figure 6-1: The cleanout cycle (http://www.rautomead.co.uk)

Aluminium bronze is a type of bronze in which aluminium is the main alloying metal added to copper, in contrast to standard bronze (copper and tin) or brass (copper and zinc). A variety of aluminium bronzes of differing compositions have found industrial use, with most ranging from 5% to 11% aluminium by weight. The remaining mass is copper, and other alloying agents, such as iron, nickel, manganese and silicon, are also sometimes added to aluminium bronzes. Aluminum bronze is the highest strength standard copper based alloy.

Aluminium bronze is most valued for it’s higher strength and corrosion resitance as compared to other bronze alloys. Aluminium bronze has good corrosion resistance in both atmosphere and sea water due to the ability of aluminium to form a protective film of aluminium oxide on the metal surface. The most common applications of aluminium bronze is for cable connectors, bearing welding wire, guitar string .

In this study, experimental work to produce 10 mm diameter aluminium-bronze rod (Cu-AL10%-Fe1%) were performed using RS80 vertically upward casting machine to evaluate the effect of cleanout cycle (build-up oxide aluminium) on tensile strength, elongation percentage and surface finish of aluminium-bronze alloys at two different run speed.

Cu-AL10%-Fe1%) is used for welding or brazing mostly for the automotive market, it is used to braze steel components together. But alternate uses also include off shore aplications because of the very good corrosion resistance and high tensile strength.

A tensile test at room temperature was carried out according to ASTM standard. The test specimens were also prepared according to ASTM standard. From created data, the percentage elongation of each sample, as well as the ultimate tensile strength, was then calculated. Table 6-6 shows the samples tested in this experiment.

Table 6-6: Aluminum bronze samples tested in this research

Sample	Rod dia. (mm)	Die	Pull Dist. (mm)	Pull Dwell (Sec)	Accl. (Sec)	Decl. (Sec)	Casting Speed (mm/min)	Water Flow Rate (ltrs/min)	Cleanout Cycle
Cast 1	10	Graphite	8	0	0.04	0.04	300	30	No
Cast 2	10	Graphite	8	0	0.04	0.04	1450	30	Yes

6.3.7 Continuous Casting Direction (Horizontal / Vertical)

Pure copper is a very good conductor of both electricity and heat. The best way to increase the electrical and thermal conductivity of copper is to decrease the impurity levels. The existence of impurities and all common alloying elements, except for silver, will decrease the electrical and thermal conductivity of copper. As the amount of the second element increases, the electrical conductivity of the alloy decreases. Silver could increase electrical and thermal conductivity of copper. Although silver is the most electrically conductive element, copper and gold are more commonly used in wiring and electronics. Copper is used because it is less expensive.

Wire and cables are very important for electrical applications to input or output electrical power and data signals. Therefore, it is necessary for wires and cables to have high electrical conductivity, low current loss and high anti-interface.

In order to enhance the electrical conductivity of wire and cables, materials such as pure copper or pure silver could use but these are very soft and difficult to refine the. So, CuAg alloy are alternative alloy for the specific application.

CuAg alloys have high electrical conductivity, high thermal conductivity, excellent formability, good weldability, excellent machinability, excellent erosion resistance and resistance to hydrogen embrittlement.

Drawing wire and copper silver core wire manufacturing are two common technology for producing this alloy. Continuous casting is an alternative method for producing copper silver length wire.

The most common continuous casting methods are horizontal and vertical. The selection of continuous casting types is dependent on the various parameters such as productivity rate, the materials, forms, shapes and dimensions of the final products. One of the purposes of this work was to experimentally investigate the dependency of the continuous casting types and mechanical properties of continuous cast copper alloys. The cast trial was attempted using a standard upward and horizontal continuous casting machine. The alloy was 2% Ag balance Cu. The trial produced 12.5mm diameter samples vertically and then horizontally.

Alloy contents are summarised in Table 6-7. In this study, two batches of samples were cast using different continuous casting types. Then, to investigate the casting type's effect on the mechanical properties of CuAg alloy, a tensile test at room temperature was carried out according to ASTM standard.

To evaluate the mechanical properties of cast one and cast two, the tensile test was performed to investigate the tensile strength (MPa) of the material as well as to find the ductility in terms of elongation percentage of the alloy.

The test specimens were prepared according to ASTM standardss, consistent with the other parameters. The specimens were tested using a computerised universal testing machine (Make: Instron; Model: 4204). Three samples were selected and an average taken.

Table 6-7: CuAg samples tested in this research

Sample	Rod dia. (mm)	Die	Pull Dist. (mm)	Pull Dwell (Sec)	Accl. (Sec)	Decl. (Sec)	Casting Speed (mm/min)	Water Flow Rate (ltrs/min)	Casting direction
Cast 1	12.5	Graphite	5	0.1	0.002	0.002	300	50	Horizontal
Cast 2	12.5	Graphite	5	0.1	0.002	0.002	300	50	Vertccal

6.3.8 Super-cooler Size

Previouly copper cadmium used for railway industry such as trolley wire but copper cadmium was banned in Europe for toxicity reasons as an alloying elements. It has been previously reported that, CuMg is the best alternative alloying element for this application which has good conductivity, tension and acceptable drawability. Additions of 0.1 to 0.7% of magnesium to copper in a workable solid solution produced a strengthened alloy with good electrical conductivity.

The alloy in this trial was 0.18% Mg balance Cu. The trial produced a vertically upward cast 15 mm diameter sample coil. Tensile strength and elongation percentage of continuous casting was investigated by a universal tensile machine. Three samples were selected and an average was taken.

Solidification of metal/alloys in the continuous casting process is controlled by it's cooling system (supercooler). Historically, Rautomead use a small supercooler (48mm) for the smaller casting rod sizes such as 8mm, 10mm or 12mm diameter, and use a large supercooler (76mm) for the casting of larger rod sizes such as (20 – 30mm diameter). This trials was for the production of 15mm diameter rod, and the goal was to find the best supercooler.

Solidification and cooling control are key factors of the continuous casting process. In continuous casting process, as shown in Figure 2.4 (Chapter literature), at the top of crucible a die and cooler device (known as a super-cooler assembly with graphite die) is fixed vertically keeping the die immersed in molten metal.

The super cooler is cooled by re-circulation of water. The molten metal enters the die and is solidified in the shape of die bore. Super-cooler in continuous casting plays a key role in transforming heat from the mould and solidifying metal during the continuous casting of copper alloys (JIE Wan-qi, 2003).

In order to evaluate the quality of continuous casting of copper alloys, it is necessary to have a detailed knowledge of the efficiency of super-cooler size on mechanical properties of continuous cast copper alloys.

This work was performed using two different super-cooler sizes (76 mm and 48 mm). Table 6-8 provides information on the copper samples tested in this study.

Table 6-8: CuMg samples tested in this research

Sample	**Rod dia. (mm)**	**Die**	**Pull Dist. (mm)**	**Pull Dwell (Sec)**	**Accl. (Sec)**	**Decl. (Sec)**	**Casting Speed (mm/min)**	**Water Flow Rate (ltrs/min)**	**Super-Cooler Size**
Cast 1	15	Graphite	6	0.1	0.002	0.002	800	45	76mm
Cast 2	15	Graphite	6	0.1	0.002	0.002	800	45	48mm

6.4 Results and Discussion

The results is divided to eight major sections. each section described the analysis data for metallography and tensile test results.

6.4.1 Alloying Elements

The tensile tests were performed on various samples using an Introsn machine. Table 6-9 shows the results obtained from the tensile test carried out on various samples of the CuZr alloy, while Figure 6-2 depicts the relationship of the ultimate tensile strength, percentage elongation and addition of alloying elements for the alloys used in this study.

It was considered that the decrease in elongation and increase in strength of continuous cast copper-zirconium alloys were mainly dependent on the solid solubility of the particular element in copper.

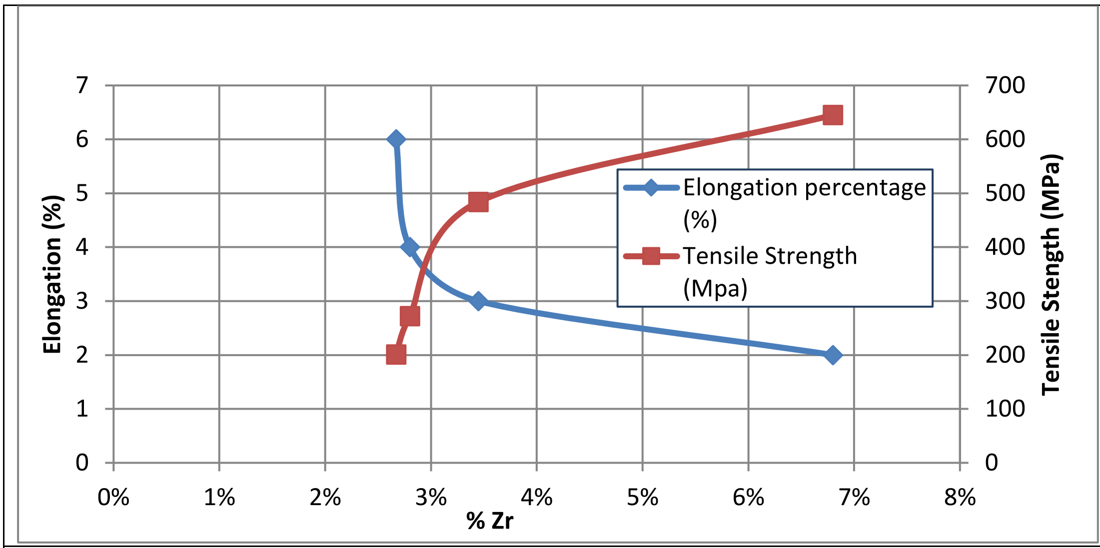


Figure 6-2: Tensile strength and elongation percentage of CuZr samples

Additives to pure copper increased its strength and reduced its elongation depending upon the element and amount in solid solution. Alloying additions could also change the microstructure of the material. The present results show that this is the most important variable, attributing about 200% of the variance on ultimate tensile strength and elongation percentage. Therefor, this study demonstrates that the choice of alloying element significantly affects the mechanical properties of continuously cast copper alloys. This is because the pure copper is soft and malleable and small amounts of an alloying element added to molten copper will completely dissolve and form as an homogeneous microstructure.

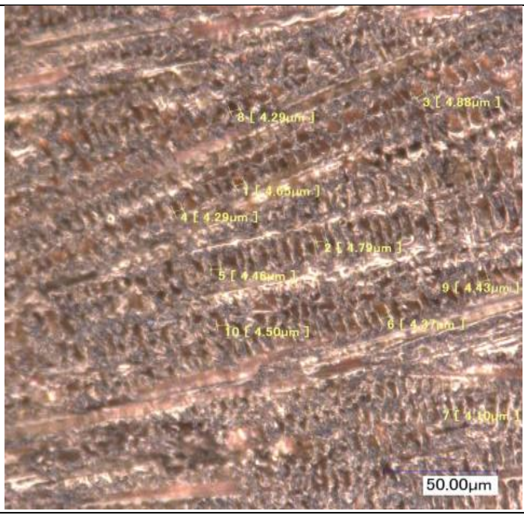
Solid solution strengthening of copper is a common procedure. Small amounts of an alloying element added to molten copper will completely dissolve and form a homogeneous microstructure (a single phase).

At some point, additional amounts of the alloying element will not dissolve; the exact amount is dependent on the solid solubility of the particular element in copper. When that solid solubility limit is exceeded, two distinct microstructures form with different compositions and hardnesses. Copper by itself is relatively soft compared with common structural metals. An alloy with zirconium added to copper, the resulting alloy is stronger and harder than either of the pure metals. In fact, zirconium can dissolve as individual atoms when added to molten copper and may remain dissolved when the material solidifies and cools down at the room temperature. However this is dependent on the solid solubility of the particular element in copper (Mouritz, 2012). The maximum solubility of zirconium metal is about 0.15% by weight. Cu-Zr alloys with zirconium contents vary from 0.01 or even less up to 0.15% and can possess exceptionally good physical and mechanical properties.

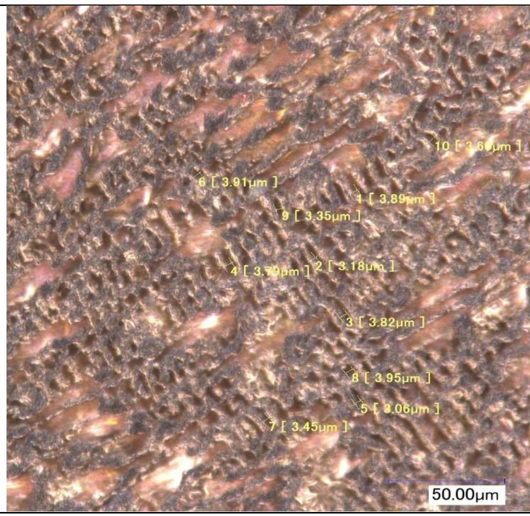
This solid solubility is at 972 centigrade degree, which is the assessed temperature of the eutectic reaction of liquid to solid. In the higher zirconium content alloys, some Cu Zr rich areas remain at the grain boundaries, providing an objectionable second phase which leads to unsoundness in the metal as well as various processing complications and difficulties (Patent No. US 2842438 , 1958). The work was continued using the metallography procedure to examine the grain structure of each specimen and the effect of alloying elements on the size of the Secondary Dendrite Arm Spacing (SDAS). This is defined as the distance between the protruding adjacent secondary arms of a dendrite and was investigated using a “KEYENCE” digital optical microscope. The result is presented in Figures 6-3 and 6-4 and Table 6-10. It has been shown that alloying elements have significant influence on the refinement of the grains.It is clearly shown, the space between dendrite arms decreased by increasing amounts of the alloying element (zirconium). Higher concentration of alloying elements will cause a precipitation of finer dendritic grain. Castings having a finer microstructure show better tensile strength. This improvement is related to a lower SDAS value. The volume fraction of the eutectic phase in these microstructure increased with an increase in the zirconium content. The cross sectional area under observation changed in structure form of dendrite types (very fine).

Table 6-9: Tensile strength and elongation percentage of CuZr samples

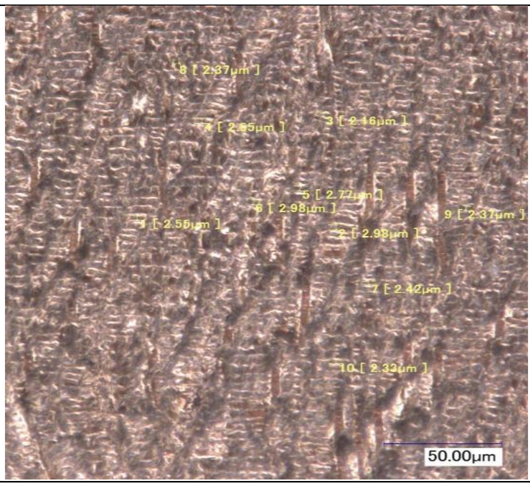
Sample	Rod Dia. (mm)	Die	Pull Dist. (mm)	Pull Dwell (sec)	Accl (sec)	Decl (sec)	Water Flow Rate (ltrs/min)	Casting Speed (mm/min)	Zr (%)	Tensile Strength (MPa)	Average Elongation Percentage (%)
Cast 1	12	Graphite	9	0.5	0.2	0.2	45	1400	2.67	201	6
Cast 1	12	Graphite	9	0.5	0.2	0.2	45	1400	2.8	272	4
Cast 1	12	Graphite	9	0.5	0.2	0.2	45	1400	3.45	484	3
Cast 1	12	Graphite	9	0.5	0.2	0.2	45	1400	6.80	645	2



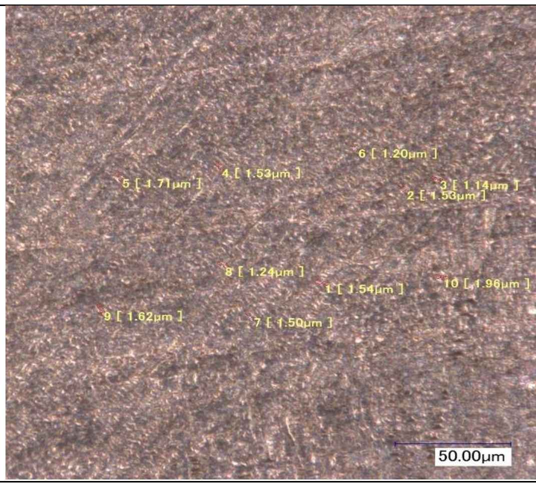
2.6% Zr



2.8% Zr



3.45% Zr



6.8% Zr

Figure 6-3: Grain structure of CuZr samples

Copper Rods

Table 6-10: Second dendrite arm space of CuZr samples

Zirconium Percentage (%)							
2.6% Zr		**2.8% Zr**		**3.45% Zr**		**6.8% Zr**	
Reading	SDAS (µm)	Reading	SDAS (µm)	Reading	SDAS (µm)	Reading	SDAS (µm)
1	4.65	1	3.89	1	2.55	1	1.54
2	4.79	2	3.18	2	2.98	2	1.53
3	4.88	3	3.82	3	2.16	3	1.14
4	4.65	4	3.79	4	2.55	4	1.53
5	4.46	5	3.06	5	2.77	5	1.71
6	4.37	6	3.91	6	2.98	6	1.2
7	4.1	7	3.45	7	2.42	7	1.5
8	4.29	8	3.98	8	2.37	8	1.24
9	4.43	9	3.35	9	2.37	9	1.62
10	4.5	10	3.61	10	2.33	10	1.96

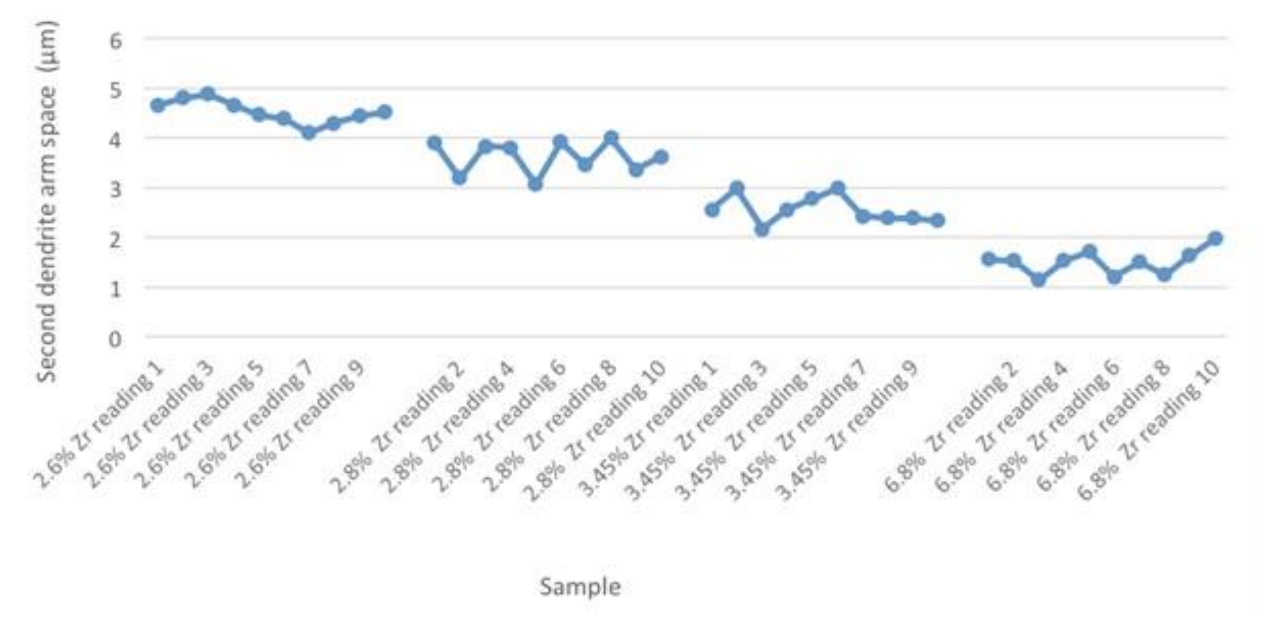


Figure 6-4: Second dendrite arm space of CuZr samples

The vertical upward continuous casting method provides a higher rate of cooling than copper mould casting, with the resulting dendritic microstructure expected to contribute to its arm-spacing refinement. This method is also exhibit good wire-drawing capability.

6.4.2 Water Flow Rate

The objective of this study was to find the effect of water flow rate on the mechanical properties of continuous cast copper rods by varying water flow rates. After cooling experiments, the tensile strength had been examined and it was found that an increase in water flow rate affected the tensile strength and elongation percentage. The results of the average elongation percentage of copper alloy samples are presented in Figure 6-5. Table 6-11 shows the tensile strength and average elongation percentage of the continuous cast copper rod samples. It can be seen that sample one has the higher elongation percentage. So the water flow rate could improve the elongation percentage of samples from 10 % to 25 %. In continuous casting process, water is used to cool the mold in the initial stages of solidification.

So water flow rate in continuous casting plays a key role in transforming heat from the mould and solidifying metal during the continuous casting of copper alloys.

It has also been previously reported that, water flow rate is one of the main process parameters that can change upon direct chill casting.

Functions of continuous casting cooling systems are;

- Formation of fine and homogeneous grain structure
- Prevent casting defect
- Prevent formation of transverse/longitudinal crack
- Provide stable and steady casting process

Because increasing the water flow in the mould increases the heat- transfer rate and thereby decreases the mould temperature (Qing Liu, 2012) and (Sengupta, 2005).

Water-cooling affects the product quality by (1) controlling the heat removal rate that creates and cools the solid shell and (2) generating thermal stresses and strains inside the solidified metal (Sengupta, 2005).

When the cooling rate is slow, some of the large clusters of atoms in the liquid develop interfaces and become the nuclei for the solid grains that are to form. During solidification the first nuclei increase in size as more and more atoms transfer from the liquid state to the growing solid.

Eventually all the liquid transforms and large grains develop. The grain boundaries represent the meeting points of growth from the various nuclei initially formed.

A low cooling rate results in less homogeneous micro-structure. On the other hand, when the cooling rate is fast, many more clusters develop and each grows rapidly. As a result, more grains form and the grain size in the solid metal is finer (William O Alexander & Bradbury E. J., 1985) and (Tadeusz Knych et al, 2011).

The effect of water flow rate on the structure of the continuous cast copper rod is illustrated in Figure 6-6. From these figures, it can be observed that fine grains can be achieved by increasing the water flow rate. Water flow rate is known to affect the structure formation during solidification.

This is because of its influence on the cooling condition. So, it was observed that the cooling rate had a very significant effect on the grain size of rods. This observation is defined with the following phenomena:

- Faster cooling results in large values of growth velocity, which results in an increase in the number of effective nucleants and a finer grain size.
- Faster cooling results in an increase of the (a) degree of constitutional and (b) amount of undercooling, which results in fine grain structure.

As well as the above phenomena, water-cooling plays a major role in extracting heat from both the casting die and the solidifying metal during the continuous casting procedure.

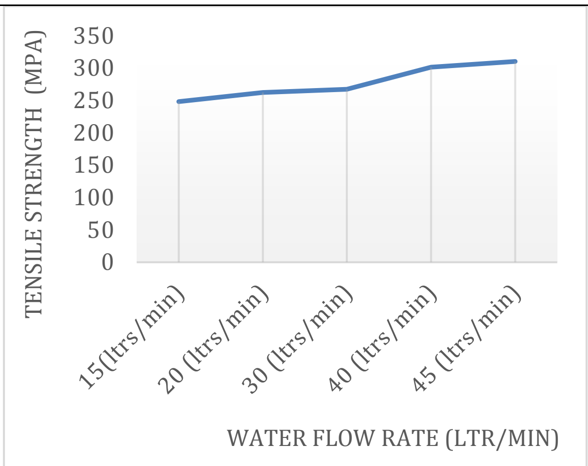
Readings of water out (˚C) and water in (˚C) were taken. By increasing the water flow rate from 15 to 45 (ltr/min) the water in temperature dropped from 24.9˚C to 23.7˚C.

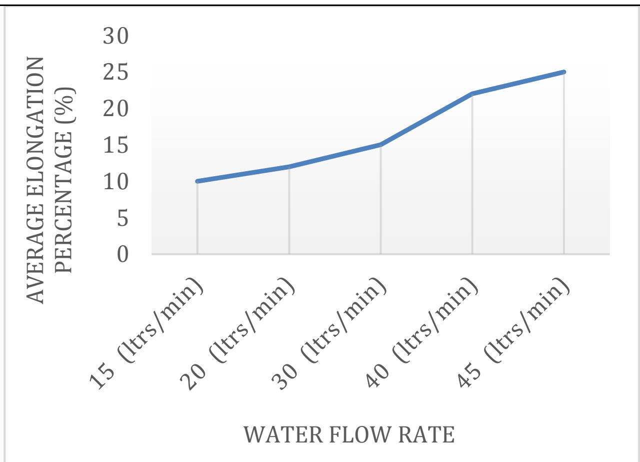
Also water out increased from 29.8˚C to 41˚C by decreasing the water flow rate from 45 ltr/min to 15 ltr/min.

As a summary, all the phenomena mentioned above confirm that water flow rate has an important impact on the physical and mechanical properties of continuous cast copper alloy (Jingchen, 2015) and (L.A. Dobrzañski, 2007).

Table 6-11: Average elongation percentage of CuSnP samples

Sample	Tensile Strength (MPa) reading 1	Tensile Strength (MPa) reading 2	Tensile Strength (MPa) reading 3	Elongation Percentage (%) reading 1	Elongation Percentage (%) reading 2	Elongation Percentage (%) reading 3	Average Tensile Strength (MPa)	Average Elongation Percentage (%)	standard deviation (tensile strength)	standard deviation (elongation percentage)
1	309	310	311	10	9	11	310	10.00	1	1
2	300	302	302	12	11	13	301.33	12	1.155	1
3	266	268	268	16	15	15	267.33	15.33	1.155	0.577
4	261	263	262	23	22	22	262	22.33	1	0.577
5	248	247	249	25	24	26	248	25.00	1	1



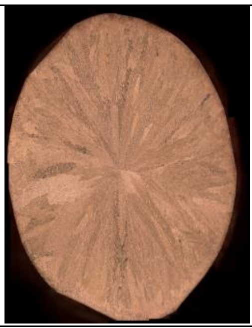


Tensile strength | Elongation percentage

Figure 6-5: Tensile strength and elongation percentage of CuSnP samples


15 (ltrs/min)


20 (ltrs/min)


30 (ltrs/min)


40 (ltrs/min)

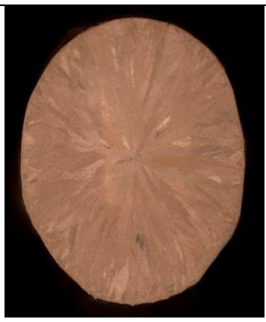

45 (ltrs/min)

Figure 6-6: Comparison grain structure of CuSnP samples

6.4.3 Casting Speed

In continuous casting process, the casting speed is one of the most important parameters that influence the metallurgical properties of cast metals.On the other hand, the casting speed, which is directly related to the productivity, is one of the most important parameters for continuous casting. So it is very important to pay attention to a proper determination of the casting speed.

The aim of this section was to investigate the impact of the casting speed on the mechanical properties of continuous cast OFCu copper rods.

Although casting speed can be calculated as a combination of steps i.e pulling time, dwell time, push back and acceleration/deceleration time, this calculation doesn’t affect the theoretical vagaries of the servo system.

For this reason, in this research the casting speed is calculated by physical measurement of the cast rod over the specified time e.g mm/min or m/min.To study the effect of casting speed in continuous casting of copper alloys, investigation has been performed with four different casting speeds. Mechanical properties of copper alloy samples (ranging from low to high casting speeds) were tested, and then the results were analysed as shown in the following Table 6-12 and Figure 6-7.

A strong correlation of the tensile strength and elongation percentage with the casting speed was observed. For oxygen free copper obtained under industrial conditions, an increase in tensile strength was observed with a decrease of casting speed.

For the material obtained at a casting speed of 2500 mm/min., the value of tensile strength was equal to approx. 178 MPa. However, for the oxygen free copper sample cast at a higher speed of 7800 mm/min., tensile strength was at a lower level of 168 MPa.

This was a significant difference, taking into account only the change of casting speed with no difference in the chemical composition of the material as well as the general method of production. It was also found that the casting speed could improve the elongation of samples from 34 % expanding to 41 %.

The reason for this huge improvement of elongation and significant difference on tensile strength is because the casting speed affects the structure formation during the solidification. This is because of influence on cooling condition, which could increase the mushy zone thickness. The region where dendrites (columnar or equiaxed) and the liquid phase coexist is called mushy zone.

The other reason for this is increasing casting speed leads to a change in the heat conduction and solidification condition, which results in making it possible to obtain a structure with finer grains. This is based on a thermal change because the higher the casting speed gets the faster the material goes from liquid to solid.

Figures 6-8 and 6-9 show cross and longitudinal sections of continuously cast rods after cutting, polishing and etching solidified at four different pulling speeds, from which it can be seen that, in the cross section, the grains are radial from the surface to the centre and in the longitudinal section, there is a centre line.

By comparing the metallurgical and mechanical properties of OFCu copper rods it can be concluded that the mechanical properties have correlation with grain size and high mechanical properties are achieved by small grain structure.

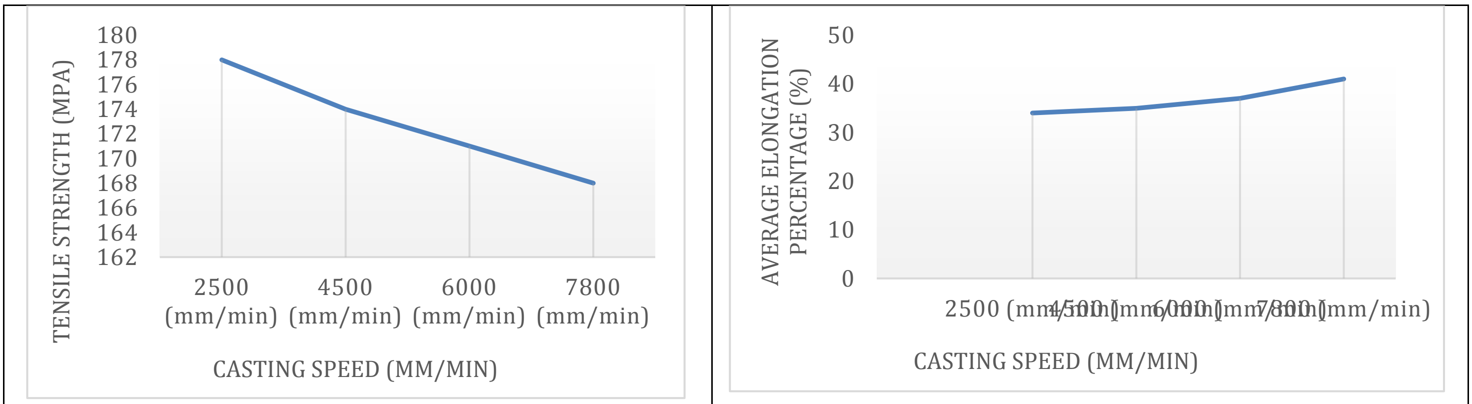
By observing the cross section of samples, it can be clearly seen that, when casting speed was increased from 2500 mm/min to 7800 mm/min, significant reduction of grain structure were observed. With an increasing of the casting speed, the grain structure tends to become finer in structure.

Longitudinal section shows, at low casting speeds (2500 mm/min), the columnar grains have a tendency to align along the longitudinal axis of the rod whereas, at higher casting speed (7800 mm/min), they grow more or less perpendicularly to the rod surface. This observation is because faster cooling results in increasing the amount of grain boundaries.

It is known from the above observation on the metallography analysis of grains that the number of columnar grains increases after grain refining by increasing the casting speed. As is well known, smaller grains have greater ratios of surface area to volume, which means a bigger ratio of grain boundaries to dislocations. (Zhiliang NING, 2007) and (Pryds, 2000).

Table 6-12: Tensile strength and average elongation percentage of OFCu samples

Sample	Tensile Strength (MPa) reading 1	Tensile Strength (MPa) reading 2	Tensile Strength (MPa) reading 3	Elongation Percentage (%) reading 1	Elongation Percentage (%) reading 2	Elongation Percentage (%) reading 3	Average Tensile Strength (MPa)	Average Elongation Percentage (%)	standard deviation (tensile strength)	standard deviation (elongation percentage)
1	178	177	178	34	33	34	178	33.67	0.577	0.577
2	174	174	173	34	36	35	173.67	35	0.577	1
3	171	170	172	37	37	36	171.00	36.67	1	0.577
4	168	168	169	42	41	40	168	41.00	0.577	1



Tensile strength | Elongation percentage

Figure 6-7: Tensile strength and elongation percentage of OFCu samples

2500 (mm/min)	4500 (mm/min)	6000 (mm/min)	7800 (mm/min)

Figure 6-8: Comparison grain structure of OFCu samples (Cross section)

2500 (mm/min)	4500 (mm/min)	6000 (mm/min)	7800 (mm/min)

Figure 6-9: Comparison grain structure of OFCu samples (Longitudinal section)

As a summary, it was found that the average size of columnar grain in the alloy decrease and grain boundary turned clear and straight with increasing the casting speed. Decreasing the casting speed leads to a change in the direction of heat condition, which in consequence, results in the creation of a flat crystalisation front making it possible to obtain a structure with grains parallel to the axis of the cast material.

Cooling rate has also a great influence on the formation of various defects within the cast product. So, an appropriate control of the strand cooling and shell growth is to be made to have defect free continuously cast copper alloy.

6.4.4 Pull Distance

In this section, various pull for withdrawing the cast copper in the vertical direction was tried from the die. Results of the mechanical tests are presented in Table 6-13 and Figure 6-10. Figure 6-11 also shows the effect of pull distance on the elongation percentage of continuous cast copper alloys. It can be noticed that the increase of pull distance from 3mm to 6mm gives a slight increase in the elongation percentage from 31% to 37%. Increasing pull distance is equal to increasing the casting speed. It was found that the average size of columnar grain in the alloy decrease and grain boundary turned clear and straight with increasing the pulling distance.

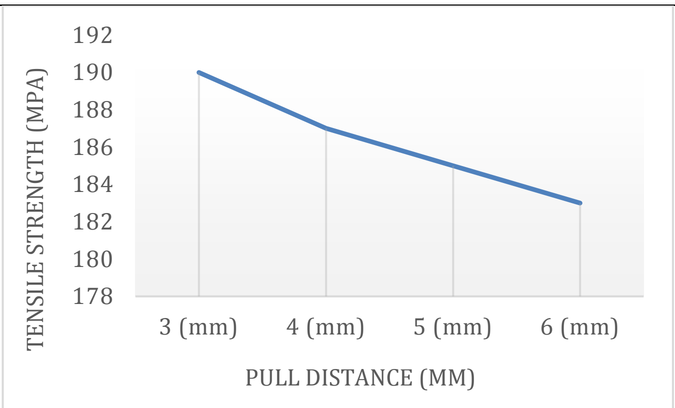
According to the equation proposed by Kumar'a decreasing the solidification time is equal to increasing the cooling rate. Many researchers mentioned that, the cooling rate is an important processing parameter that affects the mechanical behavior.

It has been reported that, the solidification time has a significant effect on the ductility of materials (Boileau, 1997).

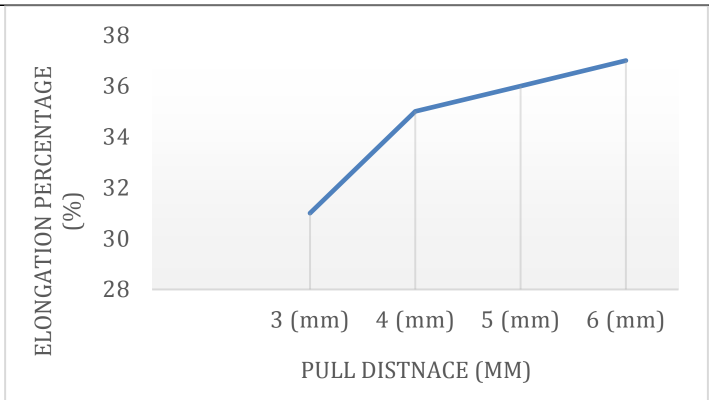
Mei et al previously reported that the faster cooling rate increased the ductility (elongation) to failure when the microstructure becomes more refined with faster cooling rate during solidification and a fine microstructure provides a better set of mechanical properties than a coarse microstructure (J.R.Davis, 2001) and (Mei, 1991). Hence, larger pull distance would improve the ductility of continuous cast copper alloy.

Table 6-13: Average elongation percentage of CuSn samples

Sample	Tensile Strength (MPa) reading 1	Tensile Strength (MPa) reading 2	Tensile Strength (MPa) reading 3	Elongation Percentage (%) reading 1	Elongation Percentage (%) reading 2	Elongation Percentage (%) reading 3	Average Tensile Strength (MPa)	Average Elongation Percentage (%)	standard deviation (tensile strength)	standard deviation (elongation percentage)
1	190	191	190	31	31	30	190	30.67	0.577	0.577
2	188	187	186	34	36	35	187.00	35.00	1	1
3	186	185	185	36	36	35	185.33	35.67	0.577	0.577
4	183	182	184	37	38	36	183	37.00	1	1



Tensile strength

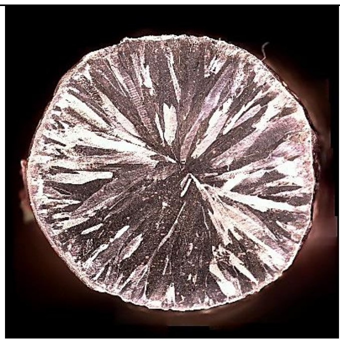


Elongation percentage

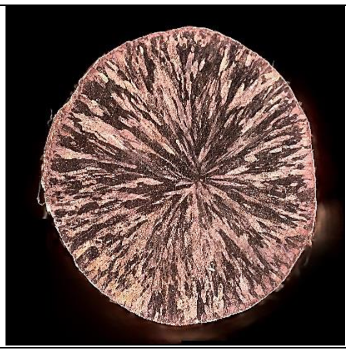
Figure 6-10: Tensile strength and elongation percentage of CuSn samples

3mm pull distance

4mm pull distance



5mm pull distance



6mm pull distance

Figure 6-11: Comparison grain structure of CuSn samples (Cross section)

6.4.5 Melt Temperature

The objective of this study was to find the effect of melt temperature on the mechanical properties of continuous cast copper rod by varying melt temperature.

Usually feed stock have some other elements (impurity). By casting the cathode feed stock in several degree above the copper melting temperature (1083 ºC), the oxygen is fire refined. By contacting the melt with oxygen which reacting the impurities with oxygen make some impurities oxide. But, these oxides are lighter than the liquid and then float on the surface and then can be trap and pick up as a slag. So, 1180 ºC (100 degree above the melting temperature) is a normal casting temperature of common copper alloys such as OFCu.

So, 1097 ºC, 1100 ºC, 1120 ºC and 1140 ºC are selected to see the efficiency of melting temperature on tensile strength, elongation percentage and microstructure of continuously cast OFCu copper alloys.

After experiments the tensile strength has been examined and it was found that strength of oxygen free continuous cast copper (OFCu) has changed when changing the melt temperature. It can be seen that the tensile strength drops to 169.56 MPa from 183.14 when the melt temperature is increased from 1097 ºC to 1140 ºC.

The results of average elongation percentage and tensile strength of copper alloy samples are presented in Figure 6-12 and Table 6-14. It can be seen that samples in Cast 4 have the higher elongation percentage and lower tensile strength.

Elongation of these samples are increased by 33%, 35%, 36% and 37% respectively, when the melt temperature is increased from 1097 to 1140 °C. The mechanical properties of continuous cast oxygen free copper (OFCu) can be changed by increasing the melt temperature.

The reason is because the melt temperature is one of the most important factors affecting the size of atomic clusters, as the temperature changes can influence the nucleation. In the other side, according to the relationship between the grain growth rate and degree of super-cooling, the larger the degree of super-cooling is the faster grain growth rate. So, with the increase of degree of super-cooling the grain size is decreased which then results in increasing elongation percentage.

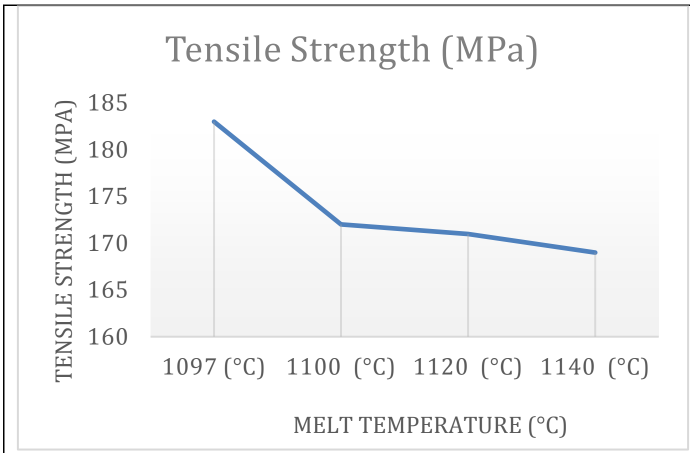
When the casting temperature is lower than optimum, the die not fill well and will solidified too rapidly. On the other hand, higher casting temperature cause shrinkage of the casting. Lower casting temperature seems to increase the formation of crack by excess material at solidification.

The casting that poured on a higher temperature means it has higher superheat. Superheat is the temperature upper the liqudus. The higher superheat will make the casting has longer time to solidified from liquid to solid and the casting will be longer. The actual density decreased with the casting temperature. This is due because the liquid with higher casting temperature has lower viscosity and turbulence is greater during the casting. Higher temperature increase the ability for dislocation to move.

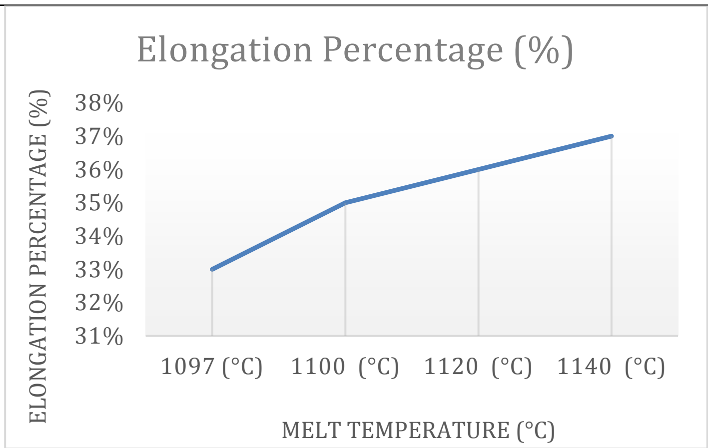
This is what cause plasctic deformation and hence ductility at lower temperature, materials become brittle because instead of the energy input to deform, is going into plastically deformation of the material. This energy going to creat new surface with crack(Jian, 2009) and (Liu et al, 2007).

Table 6-14: Tensile strength and elongation percentage of OFCu samples

Sample	Tensile Strength (MPa) reading 1	Tensile Strength (MPa) reading 2	Tensile Strength (MPa) reading 3	Elongation Percentage (%) reading 1	Elongation Percentage (%) reading 2	Elongation Percentage (%) reading 3	Average Tensile Strength (MPa)	Average Elongation Percentage (%)	standard deviation (tensile strength)	standard deviation (elongation percentage)
1	182	182	184	33	34	33	183	33.33	1.155	0.577
2	172	172	171	36	35	34	171.67	35.00	0.577	1
3	171	171	170	36	36	37	170.67	36.33	0.577	0.577
4	170	169	168	37	37	38	169	37.33	1	0.577



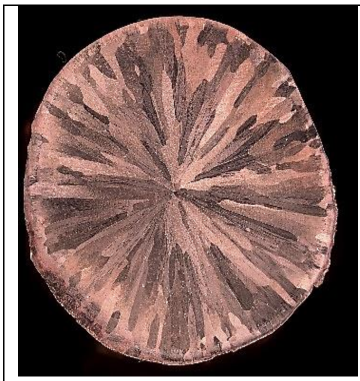
Tensile strength



Elongation percentage

Figure 6-12: Tensile strength and elongation percentage of OFCu samples

Figure 6-13 shows cross sections of continuously cast rods after cutting, polishing and etching solidified at four different melt temperatures.



1140(°C)

1120(°C)

1110(°C)

1097(°C)

Figure 6-13: Comparison grain structure of OFCu samples (Cross section)

6.4.6 Cleanout Cycles

Table 6-15 shows the results obtained from the tensile test carried out on cast 1 and cast 2. The comparison graph is also summarised in Figure 6-14. The results showed that ultimate tensile strength (UTS) of cast 2 is higher than cast 1, and that the adoption of a cleanout cycle can improve the tensile strength of aluminium bronze samples from 532 MPa to 561 MPa. It could also be observed that the value of elongation percentage of cast 2 is higher than cast 1.

When casting some copper alloys which contain certain low melting point elements, such as tin or zinc, or casting specific copper alloys like aluminium bronze, a “build up” of these elements can occur on the inside surface of the casting die where solidification is taking place which can lead to rod surface defects and breakages if left unchecked by slowly blocking the die.

The Rautomead RS – series withdrawal unit drives are fitted with cleanout cycle option designed to overcome this “build up” problem. Cleanout cycle operates in a cycle manner during the casting process and is designed such that, as the rod is being slowed down, so the solidification point of the metal being cast in the die moves towards the hot end of the die. The “build up” in the die is then attached to the solidified rod and is removed when the casting speed returns to the normal “run speed” leaving a clean die surface. Cleanout cycle gives a slight increase in the elongation percentage from 32% to 35%.

The reason is that the cleanout cycle can help to remove deposits, which may build up on the bore of casting die in the vicinity of the solidification zone. The casting speed is ramped up and down on the continuous loop. This has the effect of moving the solidification zone up and down the casting die. The other reason is oscillation mark.

In continuous casting processes, to reduce friction and avoid sticking and breakout of the liquid metal during casting, mould oscillation is required.

This oscillation is well-known to cause surface defects of continuous cast alloys i.e oscillation mark as shown in Figure 6-15 (P. Lundkvist, 2014) and (E. Takeuchi & J. K. Brimacombe, 1984).

When the liquid metal inside the casting die starts to solidify and during the solidification, surface defects called oscillation marks are formed. The oscillation marks appear as grooves perpendicular to the casting direction (Elfsberg, 2003).

And it may cause cracking and enhance the mechanical properties and yield (James M. Hill et al, 1999,). Depth of crack, width of crack and shape of crack are three main parameters used in order to describe the crack behavior. There is a correlation between oscillation mark depth and width, as deeper marks generally have a tendency to be wider (B. G. Thomas et al, 1997.) and (Tomono, 1979).

U and V shaped cracks on the surface are two main categories of oscillation marks and V shape crack is much worse compared to U shape (Vlado, 2011). To ensure the acceptability of surface finish of continuously cast aluminum bronze alloy, the depth, width and shape of the cracks must be evaluated.

In order to measure the depth and width of the surface crack of Aluminum bronze samples, the KEYENCE digital microscope was used. With the added “Measurement modes”, the VHX-1000 offers a wider range of measurements such as distance, radius or angle. In this work, the distance between two points on the screen (width or depth) is measured by specifying the points with the cursor.

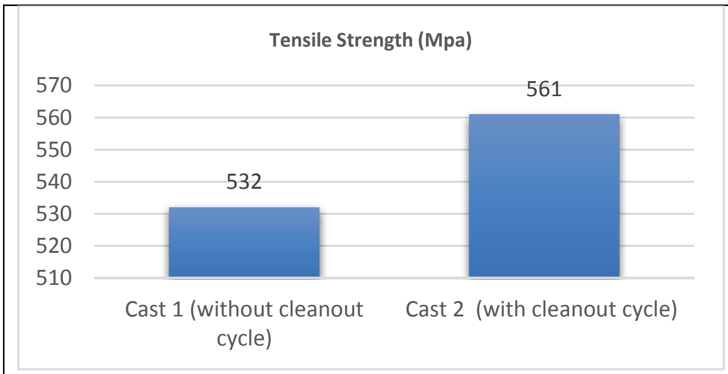
In order to prepare the samples, the samples were first cut longitudinally perpendicular to the oscillation mark and then mounted by hot mount press in epoxy resin. The longitudinal sections were machined flat, ground and polished respectively. In this work, all samples were ground first using alumina grinding paper coarse abrasive paper and subsequently wet & dry fine silicon carbide paper. The samples were then polished using diamond paste until the grinding scratches were removed. After polishing, the samples were cleaned by acetone in an ultrasonic bath and then dried with nitrogen gas. Based on the casting parameters used, and the physical sampling process and size used, only one casting cycle could be examined (per sample). However, as the casting parameters for subsequent pulses were identical, it is presumed that the crack formations will be similar (within a stated range of +/- 3% error bar), and so the following analysis is presumed to be representative of the entire cast. The pulse cycles, after polishing, are shown as “top” and “bottom” crack per casting cycle, and are presented in Figure 6-17 and 6-18 (with +/- 3% error bars).

In theory; (a) temperature, (b) strain rate and (c) state of stress are the most common factors affecting fracture. Cracks play the most important role in fracture. Crack position, crack length, crack width and crack orientation are recognized as the main crack characterizations.

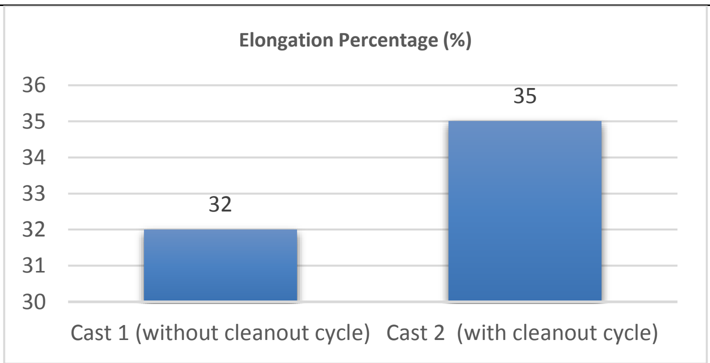
The results show that surface defects are presented in cast 1 which was without cleanout, mainly in V-shapes cracks and cast 2, which was with cleanout, mainly in U-shapes cracks. According to the fracture theory, the fracture and crack growth is strongly dependent on the crack size. V-shapes cracks in cast 1 can join each other faster compare to the U-shapes cracks in cast 2. So the tensile strength and elongation percentage of cast 2 is better than cast 1.

Table 6-15: Tensile strength and elongation percentage of Aluminium Bronze samples

Sample	Tensile Strength (MPa) reading 1	Tensile Strength (MPa) reading 2	Tensile Strength (MPa) reading 3	Elongation Percentage (%) reading 1	Elongation Percentage (%) reading 2	Elongation Percentage (%) reading 3	Average Tensile Strength (MPa)	Average Elongation Percentage (%)	standard deviation (tensile strength)	standard deviation (elongation percentage)
1	532	533	531	32	32	33	532	32.33	1	0.577
2	561	560	561	34	35	35	560.67	34.67	0.577	0.577



Tensile strength



Elongation percentage

Figure 6-14: Tensile strength and elongation percentage of Aluminum Bronze samples

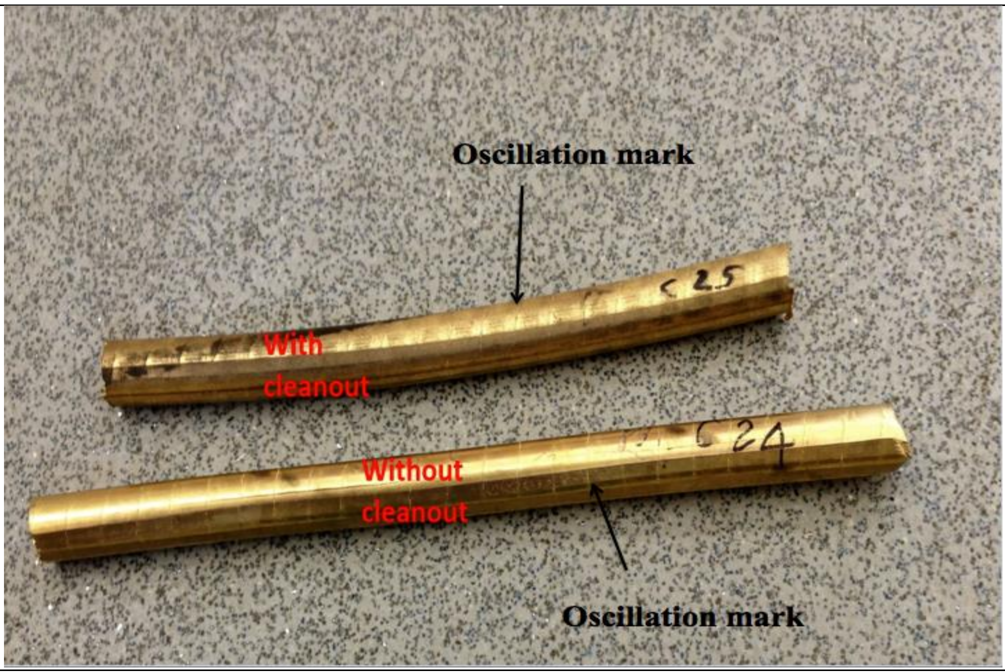


Figure 6-15: Aluminum Bronze samples

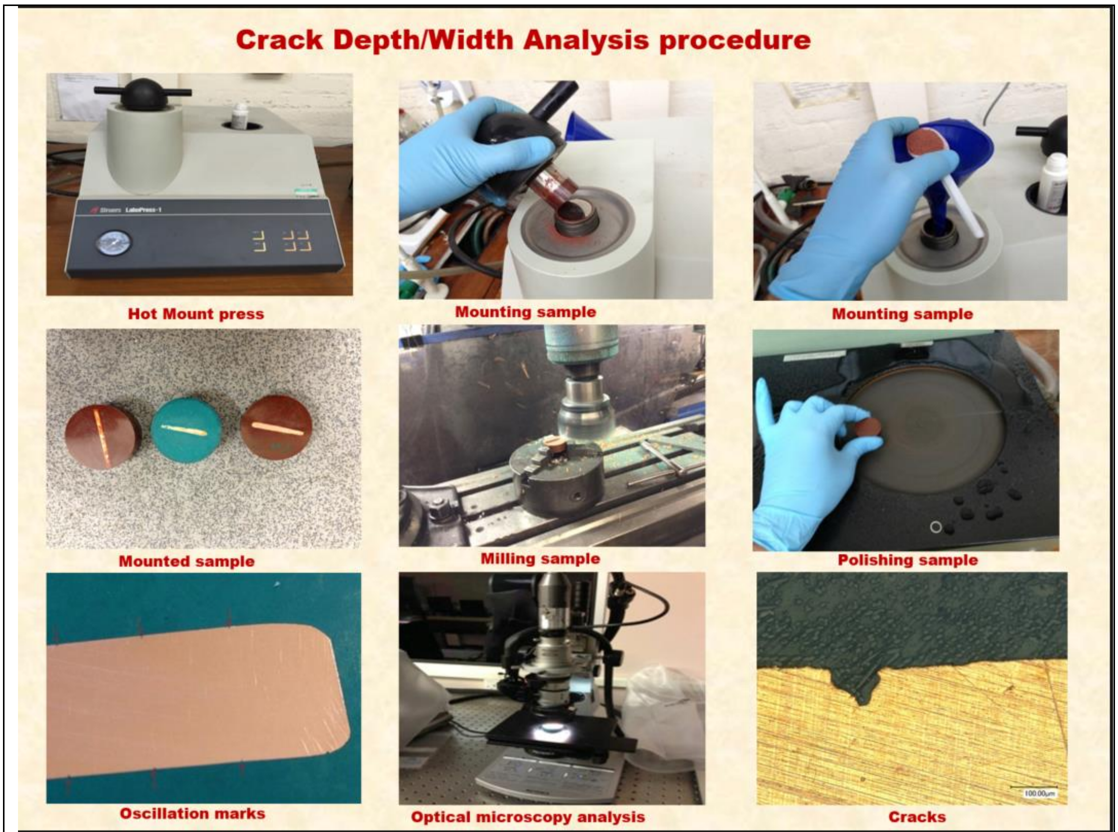


Figure 6-16: Crack depth/width analysis procedure

Copper Rods

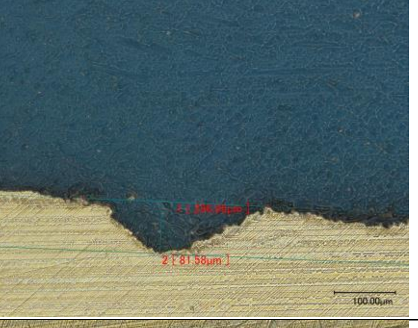
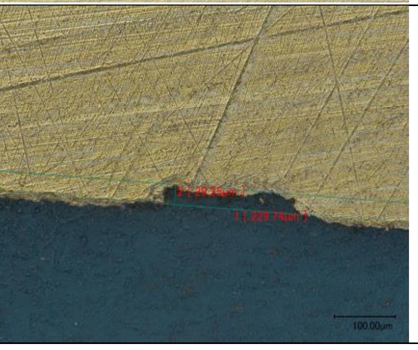
Sample	Crack position	Depth (µm)	Width (µm)	Shape	Image
Without cleanout	Top	103 (± 3%)	87 (± 3%)	Sharp (V shape)	
Without cleanout	Bottom	42 (± 3%)	49 (± 3%)	Sharp (V shape)	
With cleanout	Top	81 (± 3%)	296 (± 3%)	Dull (U shape)	
With cleanout	Bottom	29 (± 3%)	229 (± 3%)	Dull (U shape)	

Figure 6-17: Crack depth/width analysis

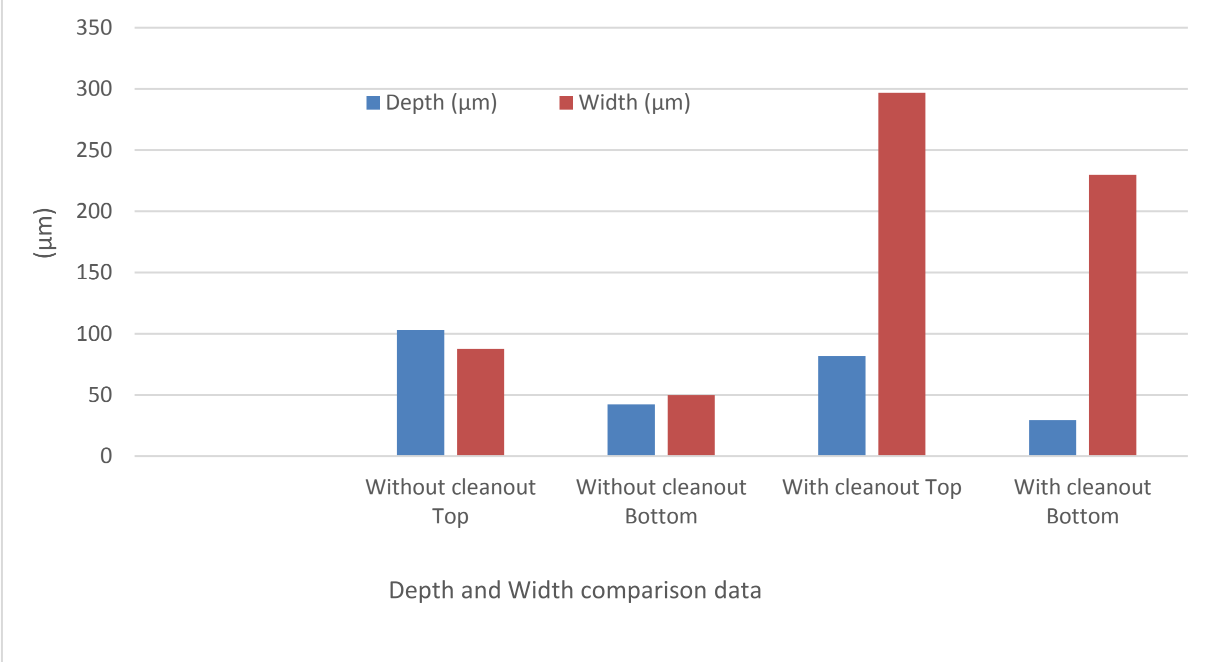


Figure 6-18: Crack depth/width analysis chart

6.4.7 Continuous Casting Direction (Horizontal / Vertical)

The objective of this study was to find the effect of continuous casting types on tensile strength and elongation percentage of continuous cast cooper rod and to identify whether the vertical or horizontal continuous casting methods has better efficiency on mechanical properties of copper alloy.

Horizontal continuous casting method has substantial cost benefits over the vertical continuous casting. This technique required lower capital investment (all the machines are on the same level), easier installation and is a more convenient technique for operators. However, the preferred casting technique is determined by the alloy and by the size range being produced.

In order to understand this aspect, this trial produced 12.5mm diameter Cu2%Ag samples vertically and then horizontally and then the samples were evaluated with a universal tensile machine for measuring the tensile strength and elongation percentage. The influence of casting types on the tensile strength and elongation percentage of Cu2%Ag is shown in Table 6-16 and Figure 6-19.

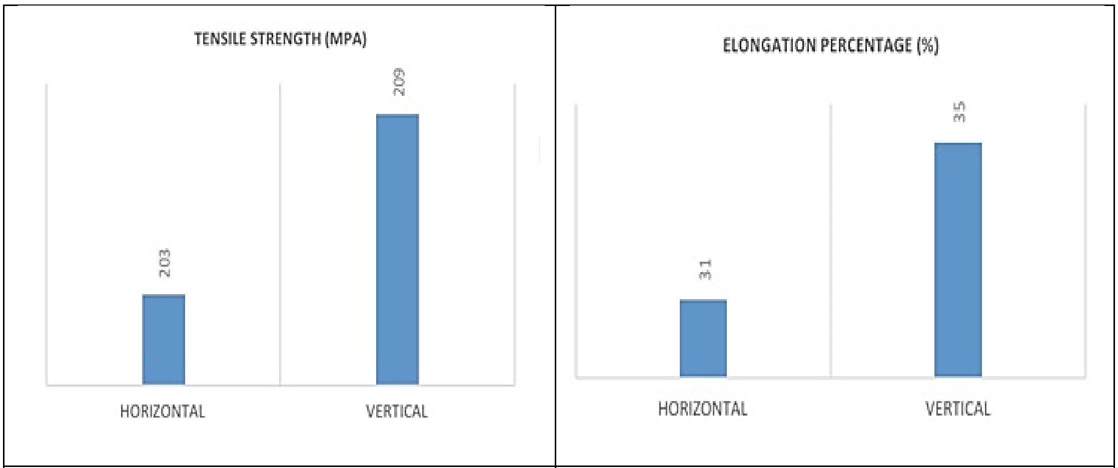
Highest UTS value was for cast 2 which cast vertically and lowest value of UTS is for cast 1 which produced horizontally. As can be seen in the following table and figures, the average elongation percentage of sample cast 2 is higher than cast 1.

Figures 6-20 and 6-21 show both the cross and longitudinal sections of continuously cast rods after cutting, polishing and etching solidified at two different casting directions. In vertical continuous casting, the molten metal flows into a water-cooled die, which is held within the crucible, and solidification of the alloy occurs.

During horizontal continuous casting, metal flows from the front of the crucible and into a water-cooled die where solidification takes place. With precise control of temperature the smaller grain structures are created. Smaller grains have greater ratios of surface area to volume, which means a bigger ratio of grain boundaries to dislocations. The more grain boundaries that occur, the higher strength. There is a slight different between the grain structure because the gravity plays a part and changing the grain structure. The bottom in horizontal casting is usually better cooled and has a finer grain. Although, metallurgical and mechanical properties of vertical casting are shown to be better than horizontal, casting of CuAg alloy was demonstrated to be easily achievable using both vertical and horizontal casting method. A visual inspection of the rod surface finish would suggest both method can produce good rod quality production.

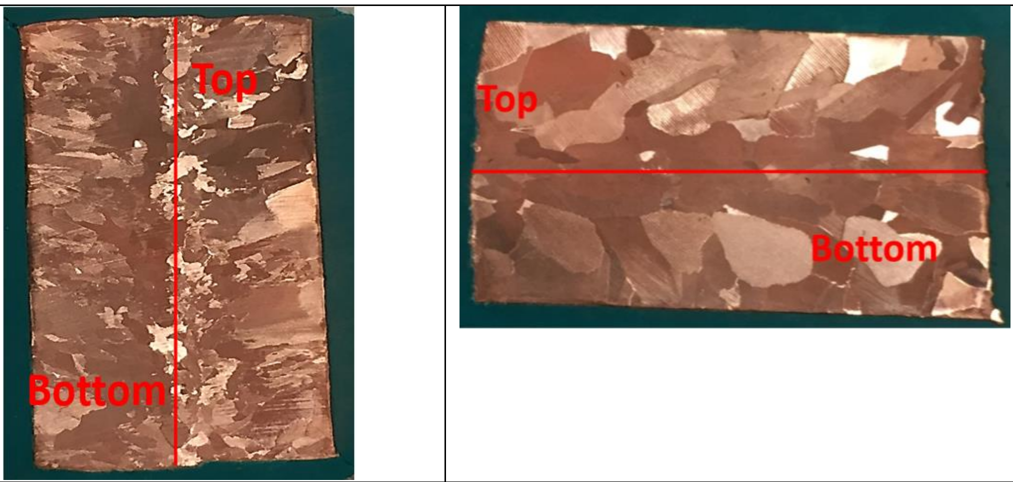
Table 6-16: Tensile strength and elongation percentage of CuAg samples

Sample	Tensile Strength (MPa) reading 1	Tensile Strength (MPa) reading 2	Tensile Strength (MPa) reading 3	Elongation Percentage (%) reading 1	Elongation Percentage (%) reading 2	Elongation Percentage (%) reading 3	Average Tensile Strength (MPa)	Average Elongation Percentage (%)	standard deviation (tensile strength)	standard deviation (elongation percentage)
1	203	204	203	32	31	31	203.33	31.33	0.577	0.577
2	209	209	210	34	35	36	209.33	35.00	0.577	1



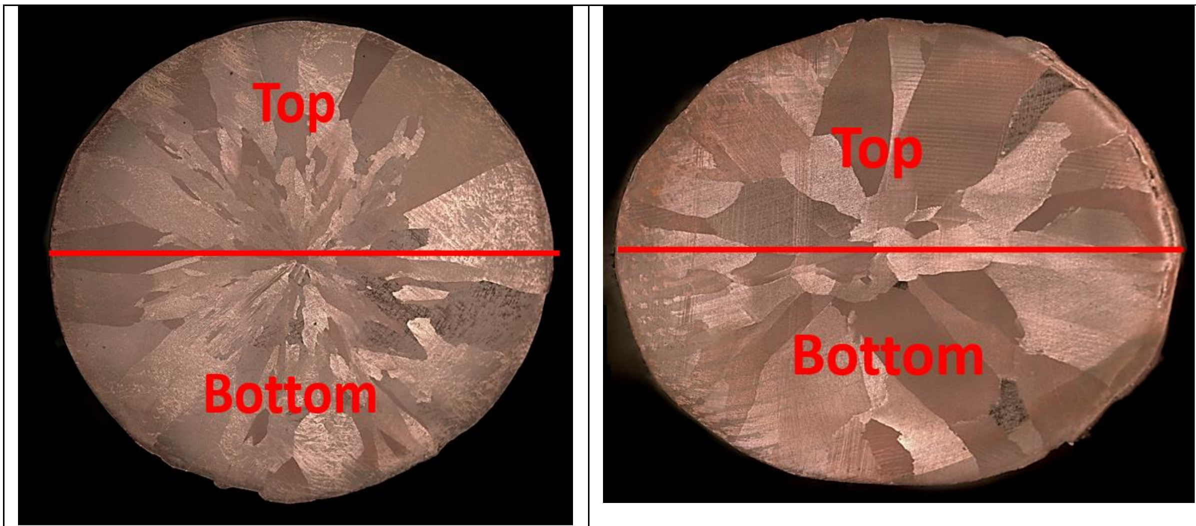
Tensile strength	Elongation percentage

Figure 6-19: Tensile strength and elongation percentage of CuAg samples



Vertical	Horizontal

Figure 6-20: Comparison grain structure of CuAg samples (Longitudinal section)



Vertical	Horizontal

Figure 6-21: Comparison grain structure of CuAg samples (Cross section)

6.4.8 Super-cooler Size

Results of the mechanical tests are presented in Table 6-17.The Figure 6-22 shows the effect of super-cooler size on the tensile strength and elongation percentage of continuous cast copper alloys. It can be noticed that the decrease of super-cooler size from 76mm to 48mm gives a slight increase in the elongation percentage from 38% to 45% and decrease tensile strength from 204 MPa to 201 MPa.

This is due to the differences between die walls of each super-cooler type. 48mm super-coolers have thinner die walls compared to 76mm super-cooler. This leads to a different cooling rate. Cooling is slower in thicker die walls compared to thinner.

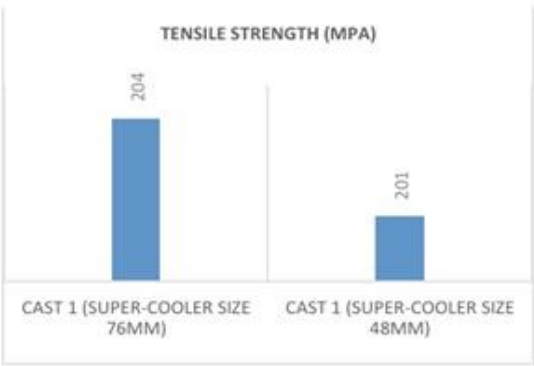
Solidification of alloys in continuous casting process is controlled by its cooling system. Cooling rate will affect the microstrucutre and is turn the mechanical properties of the materials. Figure 6-23 shows the cross sections of samples tested in this section. Slow cooling will reduce the transformation temperatures as if molten copper is cooled slowly, grains have a longer time to grow.

Thus, a large grain size is formed. Therefore, faster cooling rate will provide a harder material whereas slower cooling rate will make the softer material. Apart from this, during the slow cooling of casting CuMg alloy, the precipitated magnesium that formed in copper matrix is coarse.

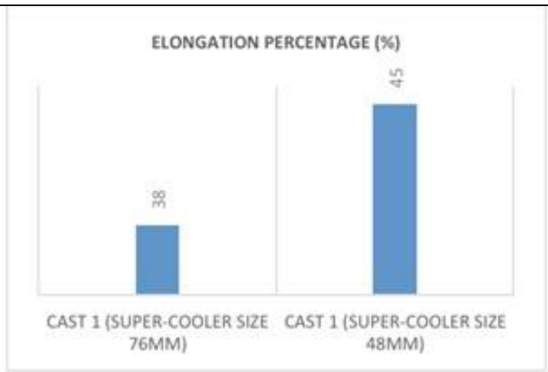
Also, when the cooling rate is slow, some of the large clusters of atoms in the liquid develop interfaces and become the nuclei for the solid grains that are to form. During solidification the first nuclei increase in size as more and more atoms transfer from the liquid state to the growing solid. Eventually all the liquid transforms and large grains develop. The grain boundaries represent the meeting points of growth from the various nuclei initially formed. When the cooling rate is fast, many more clusters develop and each grows rapidly until it meets its neighbour. As a result, more grains form and the grain size in the solid metal is finer (William O Alexander & Bradbury E. J, 1985).

Table 6-17: Tensile strength and elongation percentage of CuMg samples

Sample	Tensile Strength (MPa) reading 1	Tensile Strength (MPa) reading 2	Tensile Strength (MPa) reading 3	Elongation Percentage (%) reading 1	Elongation Percentage (%) reading 2	Elongation Percentage (%) reading 3	Average Tensile Strength (MPa)	Average Elongation Percentage (%)	standard deviation (tensile strength)	standard deviation (elongation percentage)
1	204	205	204	38	38	39	204.33	38.33	0.577	0.577
2	201	202	201	45	46	45	201.33	45.33	0.577	0.577



Tensile strength



Elongation percentage

Figure 6-22: Tensile strength and elongation percentage of CuMg samples

76mm super-cooler

48mm super-cooler

Figure 6-23: Comparison grain structure of CuMg samples

6.5 Conclusion

The effect of water flow rate, casting speed, addition of alloying elements, pull distance, melt temperature; cleanout cycling, continuous casting direction (horizontal / vertical) and super-cooler size on the mechanical properties of continuous cast copper alloys were investigated using tensile machine.

From the above experimental results, the key conclusions are:

1. Vertical upward continuous casting has good potential to be adapted to the mass production of hypoeutectic Cu-Zr alloy wires.
2. When flow rate was increased an improvement of elongation percentage was observed.
3. When casting speed increased a significant improvement of physical and mechanical properties of copper alloys were observed.
4. The addition of alloying elements could improve the tensile strength of continuous cast copper alloy. However, elongation percentage of the alloy decreases with an increase in the amount of alloying element.
5. The addition of zirconium reduces slightly the size of SDAS of continuously cast copper rod.
6. Pull distance strongly affects the physical and mechanical properties of continuous cast copper.
7. With the increasing of the casting speed, water flow rate, pulling distance the grain structure tends to become finer in continuous cast copper alloy.
8. A limitation observed in this study is that once the casting speed, water flow rate and pull distance are increased, it would result in casting fracture. At high casting speed, low pull distance and low water flow rate changing parameters should be avoided.

9. According to the relationship between the grain growth rate and degree of super-cooling, when melt temperature was increased a reduction of grain size and an improvement of elongation percentage was observed. However, tensile strength of the alloy decreases with an increase of melt temperature.
10. Cleanout cycle can help to remove deposits, which may build up on the bore of casting die in the vicinity of the solidification zone. The use of a cleanout cycle strongly affects the mechanical properties of continuous cast copper. Both elongation percentage and tensile strength improved when a cleanout cycle used.
11. Super-cooler size can enhance both physical and mechanical properties of continuous cast copper.
12. Changing continuous casting type from horizontal to vertical can improve the mechanical properties of continuous cast copper. This is due to controlling the cooling rate and changing the grain structure.
13. Casting start at low temperature and then gradually increase.
14. start casting at low speed and then gradually increase.
15. If during the casting any crack or tear observed, the temperature of the outgoing cast bar and casting speed should be decrease and after disappearing the crack or tear the temperature and speed may be increased again.
16. Large extraction materials equal to higher speed and higher productivity but sometimes lead to crack/ tear on surface of Continuous casting of alloys.
17. The cooler should be filled with water during to preheating in order to prevent distortion.

6.6 Recommendation

Based on the results obtained so far, there are some more areas need to be explored and investigated in relation to the improvement of the quality of continuous cast copper alloys as suggested below:

- Research on the influence of various die grades on mechanical properties of continuously cast copper alloy.
- Research on influence of various casting parameters on electrical conductivity of continuously cast copper alloy

Chapter 7 - Effect of Antimony Addition Relative to Microstructure, Mechanical Properties and Rod Surface Finish of Continuous Cast Lead Alloy

This chapter describes the procedure used to produce continuously cast lead alloys. In addition, tensile test analysis, optical microscopy and SEM as well as rod surface finish analysis are discussed.

7.1 Background

Pb-Sb alloys are frequently used in numerous industrial applications, such as cable sheaths, anti-friction bearings, solder and battery grids. This is due to their beneficial characteristics, such as the precipitation hardening effect, as well as their microstructural and mechanical properties (E. Jullian, 2003) , (R. Mahmudi, 2007) and (Corby G. Anderson, 2012).

Pb-Sb alloys usually can be produced by gravity casting processes (Mevlüt Şahin & Hasan Kaya, 2011) or Equal-Channel Angular Pressing (ECAP) (Figueiredo, 2006). The continuous casting process enjoys certain advantages over other processes such as the factory footprint size, cost, maintenance, energy saving, scrap rate and length size of final products.

Therefore, if the metallurgical and mechanical properties of the component produced by continuous casting are acceptable, the continuous casting process may potentially become the preferred industry manufacturing option for specific applications.

The physical and mechanical properties of lead-antimony will depend on the chemical composition of the alloy (Harmse, 2002).

Previous works have shown that, compared with other metals, lead has a much lower strength. For example, the tensile strength of mild steel is about 15 times stronger;

copper 10 times stronger; and aluminum about 6 times stronger than pure lead (Iain Thornton, 2001).

Thus pure lead is unsuitable for applications that require even adequate strength. Lead is normally considered to be unresponsive to heat treatment. Yet, some means of strengthening lead and lead alloys may be required for certain applications. Lead alloys for battery components, for example, can benefit from improved creep resistance in order to retain dimensional tolerances for the full service life. Battery grids also require improved hardness to withstand industrial handling.

The absolute melting point of lead is 327.4°C (621.3°F). Therefore, in applications in which lead is used, recovery and recrystallization processes and creep properties have great significance. Attempts to strengthen the metal by reducing the grain size or by cold working (strain hardening) have proved unsuccessful.

Small alloying additions significantly increase its strength. In solid-solution hardening of lead alloys, the rate of increase in hardness generally improves as the difference between the atomic radius of the solute and the atomic radius of lead increases.

Specifically, in one study of possible binary lead alloys it was found that the following elements, in the order listed, provided successively greater amounts of solid-solution hardening: thallium, bismuth, tin, cadmium, antimony, lithium, arsenic, calcium, zinc, copper, and barium.

Bismuth, Tin and Antimony are the most common alloying elements of lead. For example, an addition of 20% bismuth, 5% tin and 1% antimony can increase the strength of a pure lead about two times more (J. G. Thompson, 1930).

Adding sufficient quantities of antimony to produce hypoeutectic lead-antimony alloys can attain useful strengthening of lead. However an addition of antimony in lead can enhance the mechanical properties but higher antimony is avoided because of negative impact on electrochemical properties. So, lead-antimony alloys for various applications are produced at about 1-3% Sb only (Martienssen et al , 2005) and (Y Zhou, 1968).

The main aim of this study was:

(a) To investigate the possibility of melting and casting of Pb and Pb1.25% Sb using continuous casting procedure.

(b) To identify a better understanding of the effect alloying elements have on the physical and mechanical properties of continuously cast lead alloys.

7.2 Experimental Procedure

The experimental procedure of this section was include:

(a) Material prepration and casting procedure

(b) Tensile test

(c) Metallography analysis

(d) SEM/EDX

(e) Rod surface finish

7.2.1 Material Preparation and Casting Procedure

The trials were carried out on the model RS080 vertically upwards-continuous casting machine at Rautomead's premises in Dundee, UK.

This report covers sample A, which produced an 8 mm diameter rod in soft lead, and sample B, which produced an 8 mm rod in lead 1.25% antimony. The chemical composition of the cast alloy was then tested using an AMETEK spectrometer. Tensile test, metallography and SEM/EDX were used to investigate the relationship between the microstructure and mechanical properties of continuous casting fabricated Pb and Pb-Sb rod.

The main trick with melting lead-antimony alloys is to get the temperature right. This means that, the alloy is hot as to take a long time to solidify in the die. A temperature of about 370-380ºC is the proper temperature for casting of this alloy.

The representative samples analyzed in this work and their corresponding parameters are listed in Table 7-1.

Table 7-1: The lead samples tested in this research and their casting servo parameters

Sample	Rod dia (mm)	Alloy	Pull Distance (mm)	Pull Dwell (Sec)	Acceleration (Sec)	Deceleration (Sec)	Speed (mm/min)
A	8	Pb	20	0.027	0.025	0.025	7000
B	8	Pb1.25%Sb	20	0.027	0.025	0.025	7000

7.2.2 Tensile Testing

To evaluate the mechanical properties of samples, the uniaxial tensile test was used. The test specimens were prepared according to ASTM standard (ASTM E8 / E8M - 13a) and for each cast, three samples were selected and an average taken.

The tensile test was performed using a universal Instron machine (Model -4204) to investigate the tensile strength (MPa) of the material, as well as to find the ductility in terms of the elongation percentage of the alloy.

From the measured data, the tensile strength was calculated by dividing the maximum load by the original cross-sectional area of the test specimen.

7.2.3 Metallography

Because it is very soft, lead is one of the most difficult materials to prepare for metallography purposes. So, although the metallography of lead and lead alloys is not impossible, it is directly dependent on the skill and effort of the operator (Ednie, 1996) and (Slepian, 1979).

Samples for microstructural observations were cut with a clean sharp hacksaw. Sectioning of the test sample was performed carefully to avoid destroying the structure of the material. After the sample was sectioned to a convenient size, samples were then ground by using alumina grinding paper grit 220 to 1200, and then polished, beginning with 6 micron and then subsequently using 3, 1 and ¼ micron.

After polishing, the samples were cleaned by acetone in an ultrasonic cleaner and then dried with nitrogen gas. The final step used in this work, was etching the samples in an appropriate etchant solution in order to bring out the microstructure of the test sample. Etching of any soft metal such as lead and lead-alloy is the most important stage of the metallography procedure, which identifies the internal microstructure. Even a good sample preparation isn't enough to investigate the properties of alloys (J. R. Vilella & D. Beregekoff, 1927).

In accordance with ASTM E407-07 (Standard Practice for Micro-Etching Metals and Alloys), the polished samples were etched in a solution of 75ml glacial acetic acid (C_2H4O_2), 25ml of 30% concentrated hydrogen peroxide (H_2O_2) and 15ml glycerol (C_3H8O_3) for 10-30 minutes (depending on the depth of the distributed layer). Then samples were dried and cleaned with 70% concentrated nitric acid to make the crystals appear (Figure 7-1). (ASTM Standard E407 - 07) and (J. R. Vilella & D. Beregekoff, 1927).

	
Sample after etching	Sample drying with HNO_3

Figure 7-1: etching of lead alloys

7.2.4 SEM/EDX

In order to observe the morphology of lead-antimony, the etched samples were put into the stage/holder, mounted on carbon sticks, and then placed into the vacuum chamber for examination by the Scanning Electron Microscope (SEM) as well as Energy Dispersive X-ray Spectroscope (EDX) – Model the JEOL JSM7400F.

For EDX analysis, the detection limit was 0.5 to 1% by weight. A working voltage of 15KV in the SEM was used to excite the x-ray for element quantitative analysis. High magnification analysis was performed on the JEOL JSM7400F scanning electron microscope with an embedded Oxford Instrument energy dispersive X-ray analyzer (EDS).

7.2.5 Rod Surface Finish

To ensure the acceptability of surface finish of continuously cast lead alloys, the depth, width and shape of the cracks have been evaluated. In order to measure depth and width of surface crack of Pb and Pb1.25%Sb samples, the lead and lead-antimony samples were cut longitudinally perpendicular to the oscillation mark and then mounted by hot mount press in epoxy resin. The longitudinal sections were machined flat, ground and polished respectively.

After polishing, the samples were cleaned by acetone in an ultrasonic cleaner and then dried with nitrogen gas. The depth and width of the oscillation mark was examined and photographed using a “KEYENCE” digital optical microscope.

7.3. Results and Discussion

The results are divided to four major sections. These sections describe the analysis data for tensile test, metallography, SEM/EDX and rod surface finish, test respectively.

7.3.1 Tensile Testing

A small amount of alloying elements is often added to metals to improve their physical and mechanical properties. The objective of this study was to investigate the relationship between the microstructure and mechanical properties of continuous cast lead alloy. In this work, mechanical properties were monitored by a tensile test. Table 7-2 and Figure 7-2 show the average elongation and tensile strength of the continuous cast Pb and Pb1.25%Sb rod samples respectively. It can be seen that sample A (pure Pb) has a higher elongation and a lower tensile strength compared to the sample B (Pb1.25%Sb). The addition of antimony increases the tensile strength of lead casting and, on the other hand, decreases the elongation percentage of lead casting as would be expected for an alloying element.

Lead is very ductile (or malleable), that is, it can be plastically deformed, and large deformations are possible before the material breaks. In general Pure Lead is very ductile (like butter on a warm day) and it can be plastically deformed. Lead slowly deforms with time under a static load. The use of a little antimony in castings will help material flow. Antimony acts to improve the feed into a part compared to pure lead. Figure 7-3 shows optical photos of broken of fractured samples. Results showed that the fracture of lead was ductile with necking (cup and cone failure). The pb1.25%Sb is still ductile, just less so than the pure Pb (William D. Callister, 2003).

Table 7-2: Tensile test and elongation percentage results

Cast Name	**Sample No.**	**Tensile Strength (MPa)**	**Average Tensile Strength (MPa)**	**Initial Length (mm)**	**Final Length (mm)**	**Elongation Percentage (%)**	**Average Elongation Percentage (%)**
A (Lead)	1	17	17	100	143	43	41.33
	2	18		100	139	39	
	3	16		100	142	42	
B (Lead-Antimony)	1	30	29.66	100	112	12	14.33
	2	29		100	113	13	
	3	30		100	118	18	

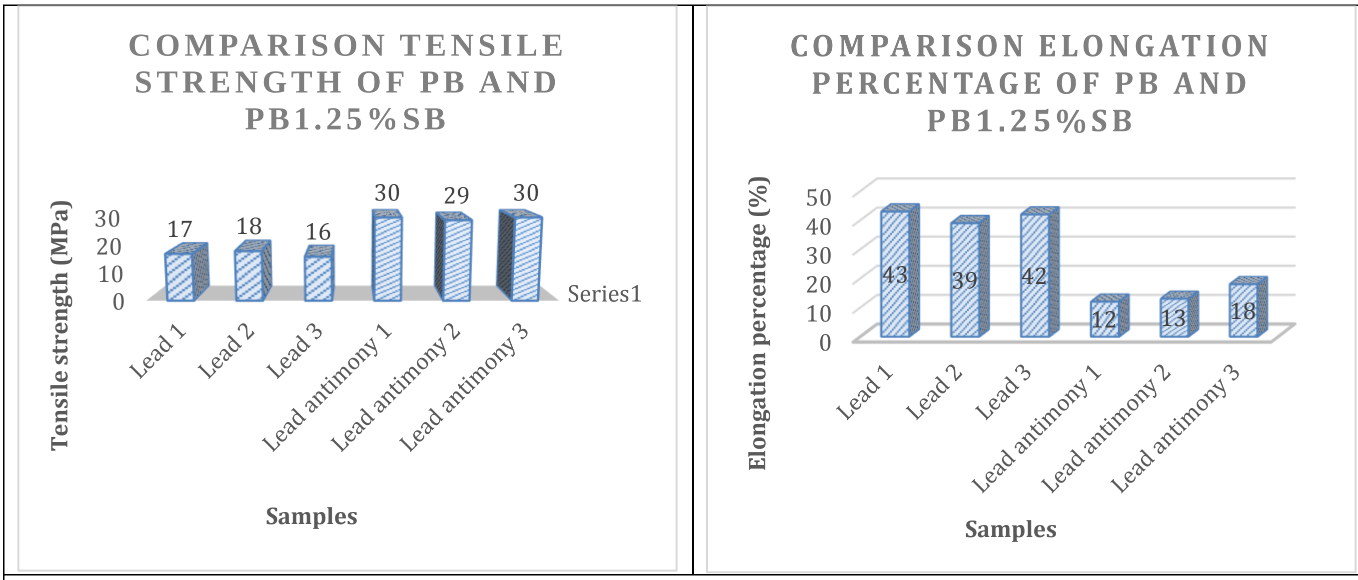


Figure 7-2: Comparison tensile strength and elongation percentage of Pb and Pb1.25%Sb

Fracture of Pb

Fracture of Pb1.25%Sb

Figure 7-3: The optical photos of the broken or fractured samples

7.3.2 Microstructure Evaluation and Average Grain Size Reading (Planimetric Method ASTM E-112)

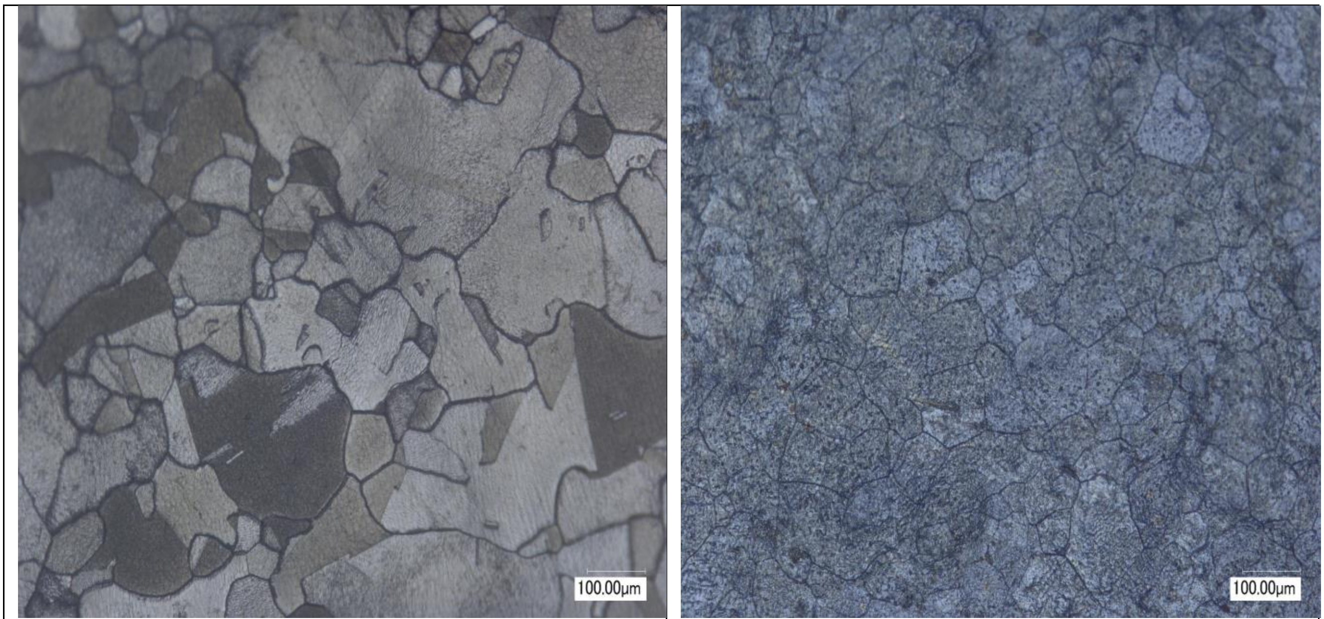
The main purpose of the present work was to investigate the effect of the addition of antimony Sb (1.25 wt%) on the structure of the lead alloys. Both the polished and then etched pure lead and antimony-added samples were observed by digital optical microscope. Figure 7-4 (a) shows the microstructure of the pure lead and Figure 7-4 (b) shows the grain structure of the lead alloy having 1.25% antimony continuous cast rod. These figures show clearly the precipitate distribution of the Pb-Sb alloy after adding antimony. As can been seen, in the antinomy added sample, there are many small dark spots with the reduced lead crystal grains. These dark spots are identified as the precipitated antinomy rich particles. As will be demonstrated in the following section, in the high magnifications SEM image observations, the dispersion of antimony rich particles within the Pb grains can be seen clearly.

The grain sizes of the homogenised, cast lead-antimony in the following figures will show a strong influence of the alloy element additions on grain size, since the casting conditions were the same for both alloys.

Additional alloying elements typically produce a fine and homogenized distribution of precipitation. Because of finer grain, there are more space precipitations. Thus, Pb1.25%Sb exhibits higher tensile strength than pure lead. Sb additions in the Pb resulted in grain refinement. A possible grain refinement was caused by increasing heating, as the melting temperature of pure lead was about 327°C and melting temperature of the Pb-Sb alloy was 380°C. So the grains within the structure recrystallize into many fine grains. This grain growth is also due to the diffusion of the solute which occurs.

In general, the smaller/finer grains, have the larger area of grain boundaries that inhibit dislocation motion and reduce the grain size. The available nucleation sites are increased. Thus, grain-size reduction typically expands toughness due to the dislocations interacting with the grain boundary, as in a larger grain there are more dislocations within the grain. There is a much greater chance for a dislocation to be stopped at a grain boundary in the smaller grain. The Hall-Petch equation explains the correlation between grain size and yield strength (William D. Callister, 2003):

This study attempts to investigate the validity of the Hall-Petch relation in the



(a) Grain structure of Pb	(b) Grain structure of Pb1.25%Sb

Figure 7-4: Grain structure of Pb and Pb1.25%Sb

continuously cast lead containing 1.25% antimony. The best way to do so is to examine the microstructure and quantify grain size.

As explained in the previous chapter, regarding to ASTM E112, there are three extensively known techniques used to measure the grain size of ground, polished and etched sections of metallographic specimens including (ASTM Standard E112 - 12):

(a) Comparison procedure

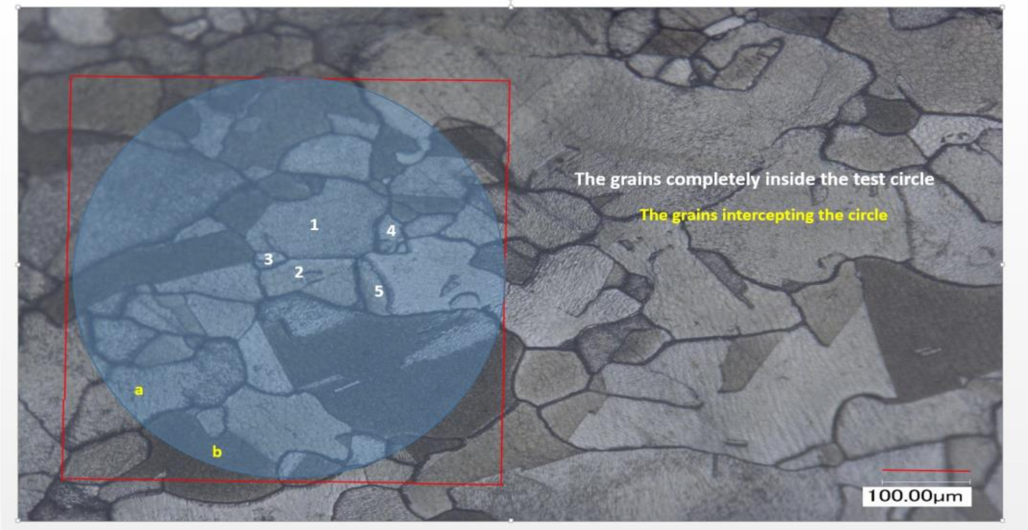
(b) Planimetric procedure

(c) Linear intercept procedure

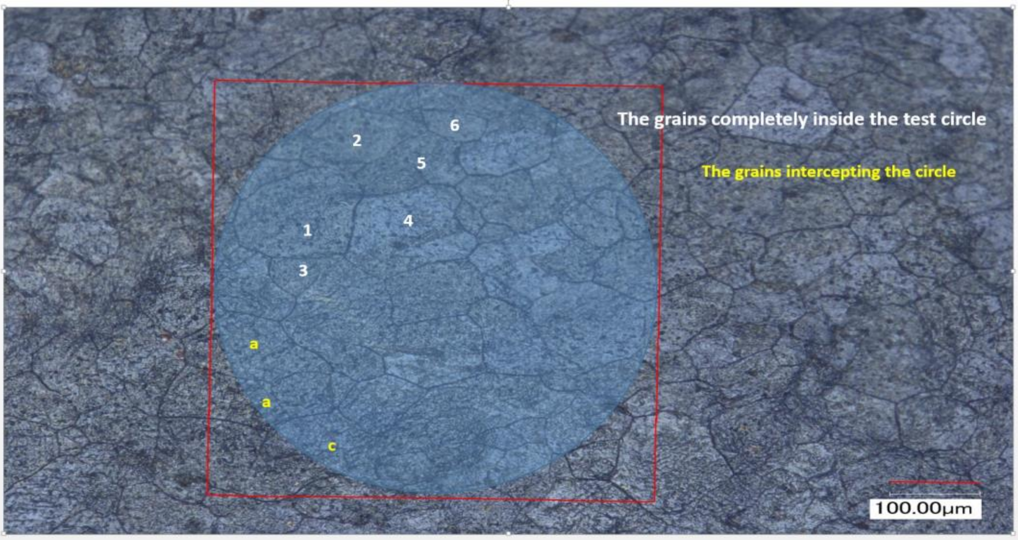
The evaluation of grain size and microstructure was determined through planimetric procedure due to the exclusive advantage of this technique which was explained in a previous chapter. The average grain sizes of samples were measured by this method. To perform this technique, a proper magnification was selected.

A circle was drawn on the image, and the grains that were located entirely inside the circle were counted and then the grains intercepting the circle were counted separately. The average grain size was calculated by using the following equation (ASTM Standard E112 - 12), (Jefferies Z et al, 1916) and (Engqvist. H & Uhrenius. B, 2003):

Figure 7-5 shows the analysis and quantification of the grain size of lead and lead 1.25%antimony by the Jeffries planimetric method.



(a) Average grain size measurement of Pb



(b) Average grain size measurement of Pb1.25%Sb

Figure 7-5: Average grain size measurement of Pb and Pb1.25%Sb

The results of average grain sizes of lead samples are presented in Table 7-3. This table shows the variations of average grain size of these two samples as discussed above.

Table 7-3: comparison average grain size of sample A and sample B

Cast Number	Alloy	Average Grain Size (mm2)	average grain per square millimetre
A	Lead	0.0053	188
B	Lead-Antimony	0.0045	223

The following section, will explain that in a lead containing about 0.44 wt% Sb the antimony is not dissolved until the temperature exceeds 100°C. It will remain undissolved at temperatures up to and somewhat above 100°C. Then, the grain growth can increase in grain size.

7.3.2.1 Lead Antimony Phase Diagram

In the phase diagram of PbSb as shown in (Figure 7-6), the Sb forms a eutectic phase with Pb. Eutectic system is for alloys with limited solubility. The melting point of eutectic alloy is lower than that of the components such as lead and antimony. Eutectic reaction is a transition from liquid to mixture of two solid phases, $\alpha + \beta$ at eutectic concentration.

Lead-antimony has a low-melting point binary eutectic alloy system. When a liquid of eutectic composition solidifies, a eutectic microstructure is formed with a layer of α and β phases. Sb rich grains are formed when the Sb concentration in PbSb alloy exceeds the solubility limit, which is only 0.44 wt. % at 100°C.(Gierlotka, 2013).

So the expectation of Lead 1.25% Antinomy based on its phase diagram is L+α structure. This will be investigated by SEM/EDX machine in the next section.

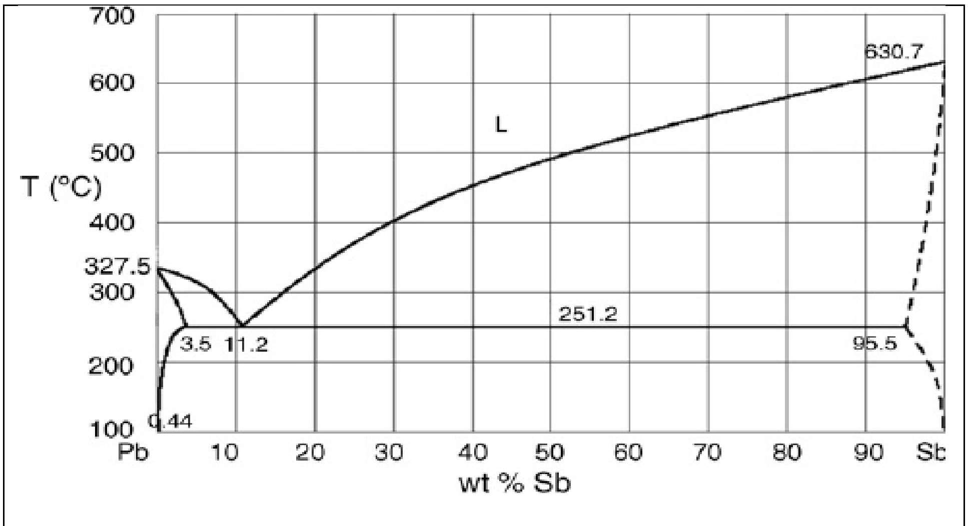


Figure 7-6: Phase diagram of Pb Pb (weight percent and atomic percent

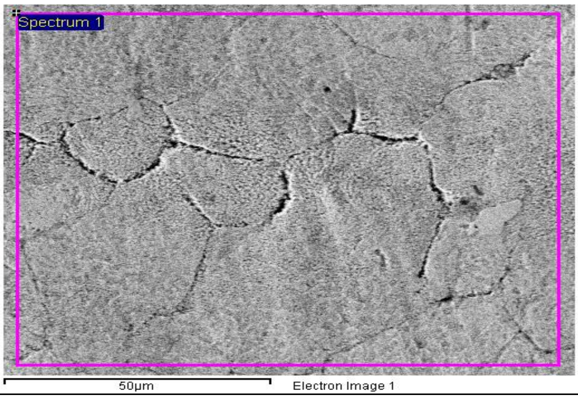
7.3.3 SEM Image Observation EDX Analysis

A JEOL JSM7400F Field Emission Scanning Electron Microscope (SEM) was used for microstructural analysis and an Energy Dispersive X-ray Spectroscopy (EDX) was performed to analyze the chemical composition of the alloys.

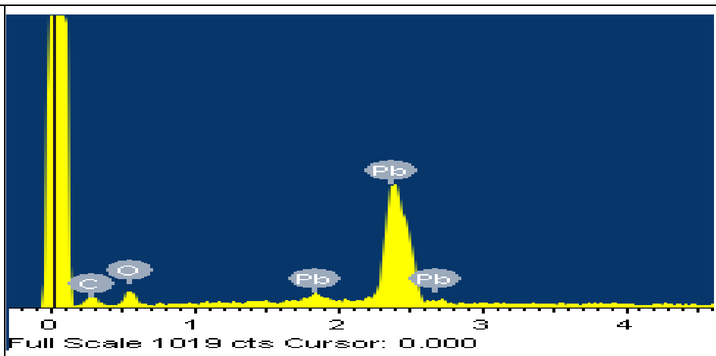
Figure 7-7 shows the electron image (an enlarged view) of both the pure lead and lead-antimony alloy in the as-cast condition, whereas it presents the similar image using the optical microscope. Figure (a) shows the microstructure (SEM image) and figure (b) illustrates the EDX analysis.

The darker regions, which are seen in more detail around the precipitates in the second image, are antimony rich regions, which are not observed in the as-cast pure lead structure. Hypoeutectic lead alloys contain less than 13% Sb, in the structure they have crystals of excess lead in form of dendrites and eutectic. Therefore, in the structure of the lead alloys is present in two structure types;

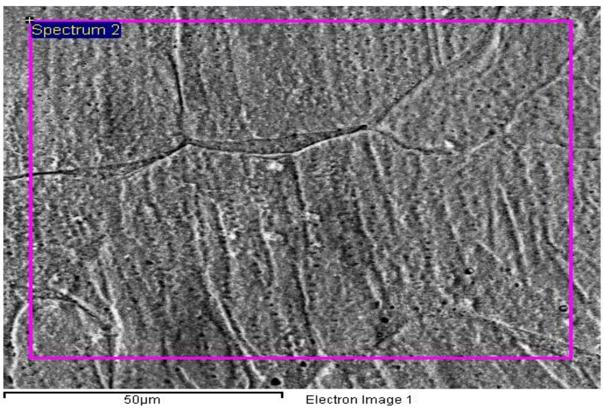
1- Large crystalinesions in the form of dendrites.
2- Smaller crystals having the form of plates participating in eutectic structure.



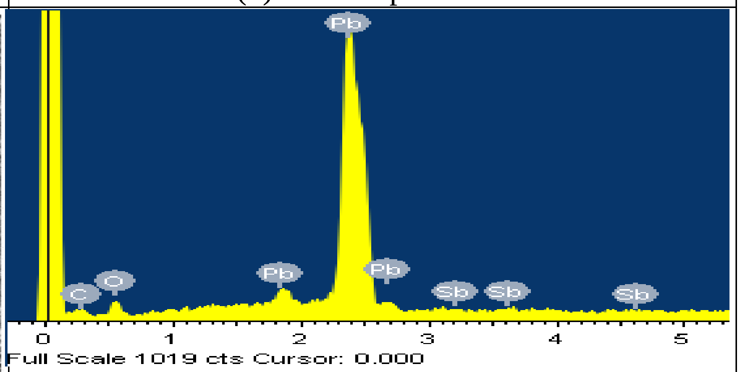
(a) SEM of pure lead



(b) EDX of pure lead



(a) SEM of Pb1.25%Sb



(b) EDX Pb1.25%Sb

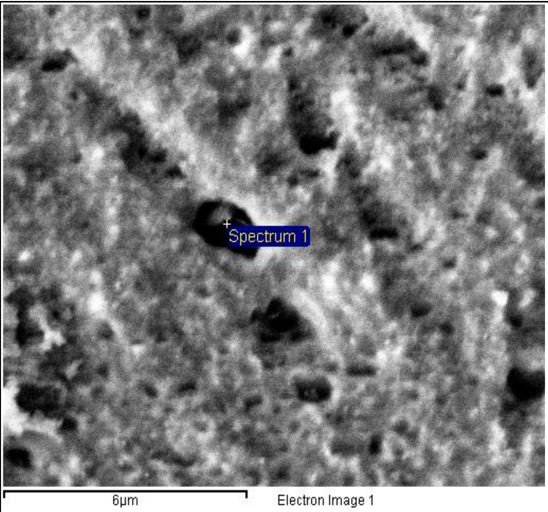
Figure 7-7: SEM and EDX of pure lead and lead 1.25% antimony

As discussed in the previous section the results from the SEM analysis, figure 7-8, demonstrate the Pb-Sb matrix (L) plus Pb (alpha) structure as expected. The Pb-Sb phase diagram shows the eutectic point of the alloy being 11.2%wt Sb. Therefor the hypoeutectic range would be up to 11.2%wt Sb and the hypereutectic range over 11.2%Sb. The alloy analysed using the SEM in figure 7-8 was within the hypoeutectic range at 1.25%wt Sb. The solubility at 100C of Sb in Pb is 0.44%wt and for 1.25%wt Sb the SEM and EDX analysis confirm the expected structure.

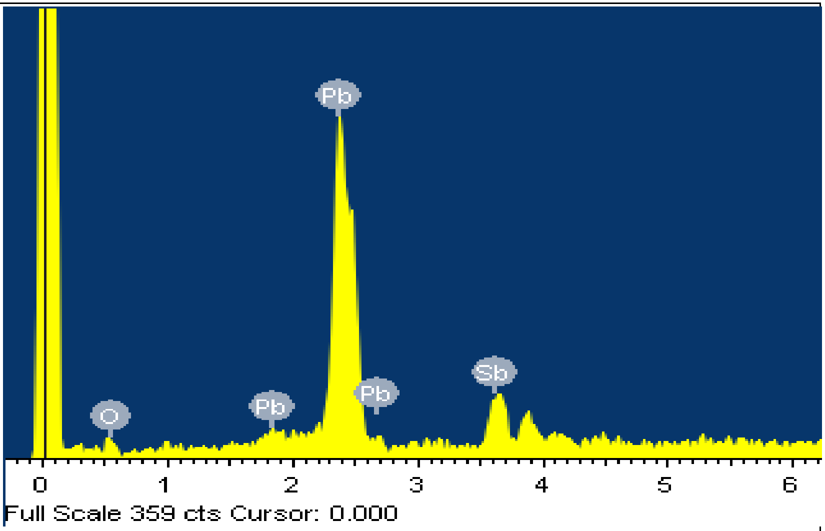
The bright phase is the lead rich matrix and the dark phase corresponds antimony rich precipitation formed in the eutectic reaction.

The mixture is slow cooled, undergoing no change in state until it reaches temperature T1, when it reaches the liquidus line, alpha phase (Lead) starts to solidify at any favourable nucleation sites. Then the alpha solidifies as dendrites, which grow to become grains of alpha. As the alloy continues to cool the existing nucleation sites will grow and further nucleation sites will continue to form within the liquid parts of the mixture. These nucleating and growing regions of solid alloy form grains and when these meet grain boundaries are formed. The primary alpha dendrites grow, which accounts for the shapes the alpha forms in cross sectional samples. As the remaining liquid cools its composition becomes richer in matrix. The composition of the solid alpha also becomes richer in matrix, as shown by the phase diagram.

These SEM/EDX observations and analysis were useful to understand the solidification process of lead 1.25% antimony alloys and to explore the relationship between the tensile strength of Pb1.25%Sb with the structure.



(a) SEM of selected point



(b) EDX of selected point

Figure 7-8 SEM and EDX of selected areas

7.3.4 Rod Surface Finish

In this work, consequently, the effect of continuous casting condition on surface roughness of lead and lead-antimony alloy rod produced by a vertical continuous casting process investigated (comparison of top and bottom of each samples). Results of the rod surface finish are presented in Table 7-4 and Figure7-9. The results show that surface defects are presented mainly in V-shapes cracks. They were about 134-145 µm deep on top, and 69-85 deep on bottom. Also, they were about 388-400 µm on top wide and 116-146 µm on bottom wide. So, the results were the same for the top and the bottom of the face. Results demonstrated that the addition of antimony doesn't affect the rod surface finish.

Table 7-4: Crack depth analysis results.

Sample	**Crack 1 Depth (µm)**	**Crack 1 Width (µm)**	**Crack Shape (V/U)**	**Crack 1 Depth (µm)**	**Crack 1 Width (µm)**	**Crack Shape (V/U)**
A	145	400	V-shape	69	116	V-shape
B	134	388	V-shape	85	146	V-shape

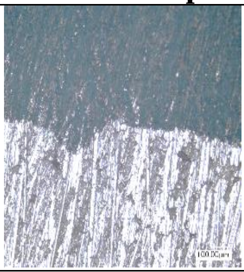
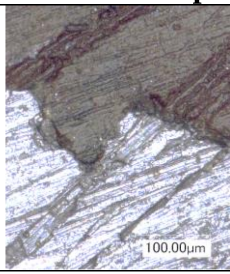
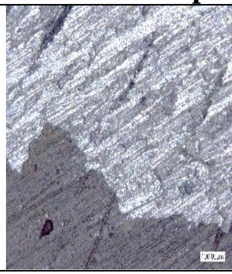
Sample	Crack 1 Shape	Crack 2 Shape	Sample	Crack 1 Shape	Crack 2 Shape
A			B		

Figure 7-9 Crack shapes

7.4. Conclusions and Future Work

This study investigated the influence of an alloying element on the microstructure and mechanical properties of lead1.25% antimony alloys. From the experimental results and their analysis, the following conclusions can be drawn:

1- Lead1.25% can be produced by continuous casting procedure without any significant problem.

2- The addition of antimony as an alloying element improves the tensile strength of the continuous cast lead alloy. Results showed that the tensile strength of the pure lead was higher as the amount of antimony increased, making tensile strength increases from 17MPa to 29MPa when 1.25 wt% Sb was added to the pure lead. So, lead containing 1.25% antimony has higher tensile strength of pure lead.

3- The addition of antimony resulted in a decrease in the elongation percentage. It was found that the addition of 1.25% antimony into the pure lead, reduces its elongation from 41% to 14%.

4- The fracture of lead was ductile with necking. The Pb1.25%Sb was still ductile, but less so than the pure Pb.

7.5. Recommendation

There are several lines of research arising from this work which should be pursued:

1- Investigation into the influence of casting speed and mechanical properties of continuous cast lead alloys.

2- Increase casting speed required more immersion depth. Efficiency of immersion depth versus tensile strength and elongation percentage could be an alternative research and development of lead trial.

3- Improving the surface finish.

4- Research on the influence of casting speed and immersion depth on surface finish of Continuous casting of lead-antimony alloys.

Chapter 8 - Investigation of the Distribution of Lead in three Different Combinations of Brass Feedstock

The following chapter presents and analyses the distribution of lead in three different combination of brass feedstock including:

- Copper granules and Zn pieces melted in an induction furnace together with elemental additions and poured into a Rautomead caster.
- Brass scrap and Zn pieces together with the balance of elemental additions melted and cast in a Rautomead caster.
- Copper scrap and Zn pieces together with the elemental additions melted and cast in Rautomead caster.

8.1 Background

Brasses cover a range of alloys of copper and zinc containing up to around 45% Zinc and constitute one of the most important groups of non-ferrous engineering materials. Brass is extensively used in numerous market applications such as screws, valves, bearings, fittings and specialty fasteners due to its beneficial corrosion resistance, thermal and electrical conductivity, formability and good mechanical properties (Sun, 2014).

Some alloying elements enhance the special characteristics of brass. Lead is one of the most important elements, which can be added to any brass to increase machinability properties with respect to low melting point of lead and very low solubility of lead in brass. However, other elements such as bismuth (Bi), tin (Sn) and arsenic (As) are used to improve some characterisation of brass (Ch.Nobel & F.Klocke , 2014) and (A. Momeni, 2015). As a particular example, tin in brass helps to prevent the segregation of bismuth from the grain boundaries. Bismuth is next to lead in the periodic table, so is added to brass as an alternative to lead have the the same efficiency but without adverse health effects. Leaded brass has excellent machinability, good strength, good corrosion resistance. Leaded brass wires remain in use for years. Thus, Lead brasses are used for their high machinability and atmospheric corrosion resistance.

Despite the advantages of using lead to improve the machinability, it must be limited because of health and environment. Evaluation of the efficiency of substitute elements in the machinability is important because of the impact on the manufacturing cost.

Leaded brass rods can be produced by continuous extrusion forming technology and continuous casting. The important disadvantage of producing a brass alloy rod by continuous extrusion forming technology is the quality of the brass alloy rod.

The use of continuous casting gives a range of advantages in comparison with continuous extrusion forming such as low energy consumption, high productivity, length size of final product, long production run capacity and cost.

Once a continuous casting machine is set-up with it's casting die in place, it can often run for 5x24 hr followed by a die change over a weekend. Where the die does not require to be changed, the machine can be left in standby mode, full of molten metal and production can be restarted when required (Li, 2014) and (Cuypers, 1987).

Continuously cast leaded brass wires are mainly use for electrical discharge machining spark erosion cutting wire, bearing connector pins wire and specific for automotive electrical wires.

Leaded brass bars with the same composition but with different combinations have been characterised in this work. Chemical composition and microstructure have been studied in order to clarify the distribution of lead.

8.1.1 Brass Phase Diagram

Figure 8-1 shows the phase diagram of brass. CuZn alloy system contains intermediate phases. Brass alloys having various Zn content are categorised into different types of brass:

- Alpha brasses (Zinc (%) <35), which contain only one phase, with face-centered cubic crystal structure. Alloys containing up to 35% Zinc are cold-working alloys with high ductility and deep drawing properties.
- Alpha-beta brasses (Zinc (%) 35-45) which contains both α and β phase; β-phase is body-cenred cubic BCC and α phase is FCC. Alloys above 35% Zinc appears plastic at high temperature imparting excellent hot-working properties.
- Beta brasses (Zinc (%) 45-50), which contain only one phase, with body-centered cubic crystal structure.

There are other types of brass such as;

- Gama brass: (Zinc (%) 33-39) and (Copper (%) 61-67).
- White brass: (Zinc (%) >50) and (Copper (%) <50).
- Cartridge brass: (Zinc (%) 30) and (Copper (%) 70).
- Gilding metal: (Zinc (%) 5) and (Copper (%) 95).

Low percent elements usually added to brass to improve various properties. As a particular example;

- Tin is added in small amounts up to about 1% to improve corrosion resistance
- Small addition of Nickel up to 3% can improve the corrosion resistance
- Arsenic is added in small amounts to inhibit dezincfication (leaching zinc from copper in an aqueous solution)
- Addition of Silicon to brass enhance the mechanical properties by increase the fluidity of the molten metal.

- Other elements such as magnesium, iron and aluminium enhance in various properties such as tensile strength.

Lead is the most common alloying element added to brass to improve the properties. Leaded brass is an alpha-beta brass with an addition of lead with excellent machinability. The addition of lead in the range of 1 to 3 wt% to the Alpha-beta brasses is made to improve machinability. Lead is often added to brass alloys to improve machinability while properties remain unchanged. The solubability of lead in brass is very low and therefore, it pricitipate as fine gloubles in the grain boundaries in the microstructure. Lead, being practically insoluble in brass in the solid state, separates out in small isolated globules uniformly distributed through the structure. Since lead has allow melting point (327.5 ºC), than the other constituents of the brass, it tend to migrate toward the grain boundaries in the form of globules as it cools form casting.

According to the previous literature, lead particle distribution is excellent in continuous cast brass structure. The objective of this study was to investigate the impact of using three different charge (Copper granules, Brass scrap and Copper scrap) on distribution of lead particle using optical microscopy and mass spectrometry to compare the distribution of lead.

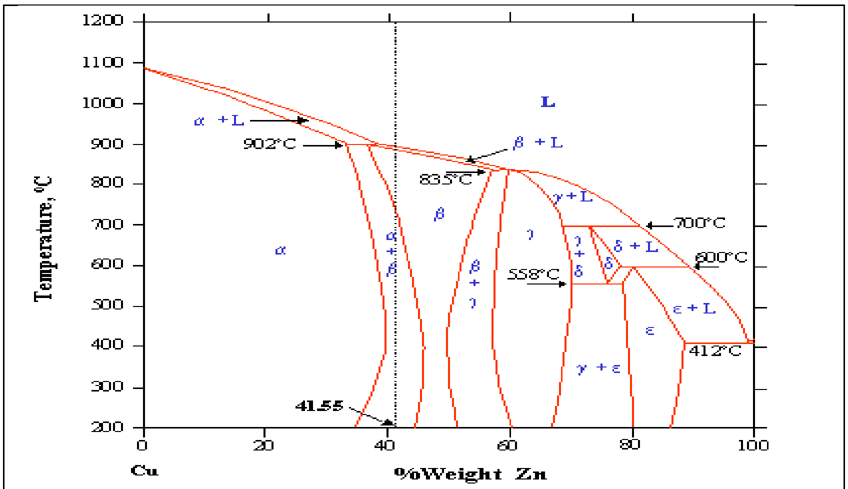


Figure 8-1: Phase diagram of brass (Copper Development Association (CDA), http://copperalliance.org.uk/)

8.2. Experimental Procedure

The experimental procedure of this section was include:

(a) Casting

(b) Metallography analysis

(c) Mass Spectrometry analysis

(d) SEM/EDX

8.2.1 Leaded Brass Samples

The representative leaded brass samples analysed in this work and their corresponding combination and information is listed in Table 8-1 to Table 8-4.

Leaded brass samples with 0.1 - 0.2% Pb contents according to Table 8-4 were used in this investigation. Nearest Alloy Designation is C28XXX (pending application with Copper Development Association - CDA). Distribution of Pb was investigated by metallography and mass spectrometry analysis.

In this work the charge was first weighed by the operator and then was melted in a graphite crucible using graphite heating element furnace technology (Rautomead horizontal continuous casting machine) as shown in Figures 8-2 and 8-3.

(a) Weighing scraps by operator	(b) Scrap

Figure 8-2: weighing by operator (http://www.lcl.com.au)

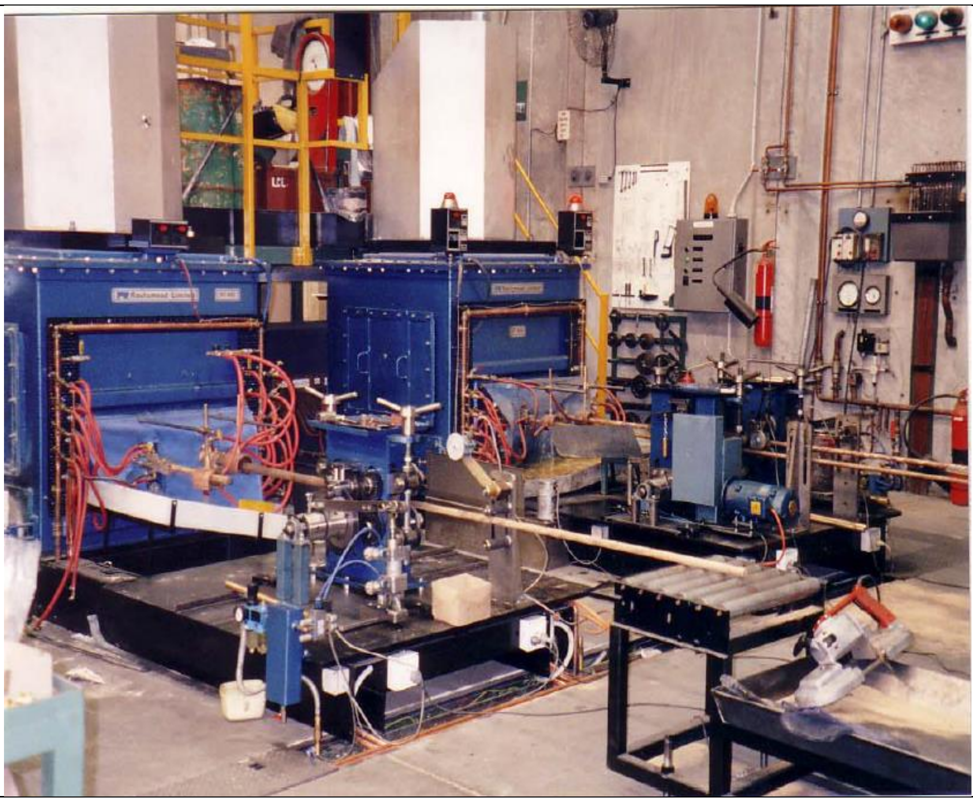


Figure 8-3: Horizontal Continuous Casting (http://www.lcl.com.au)

Table 8-1: Leaded brass samples tested in this research (http://www.lcl.com.au)

Sample Name	Combination
Sample 1	Cu granules and Zn pieces melted in an induction furnace together with elemental additions and poured into a Rautomead caster.
Sample 2	Brass scrap and Zn pieces together with the balance of elemental additions melted and cast in a Rautomead caster.
Sample 3	Cu scrap and Zn pieces together with the elemental additions melted and cast in Rautomead caster.

Table 8-2: Leaded brass samples data (http://www.lcl.com.au)

Sample Name	**Charge Weight**	**Picture of the charge**	**Picture of the Zn piece**
Sample 1	Granules into approximately 5kg briquettes Zn in 25kg slabs		
Sample 2	Various brass scrap from approximately 500g to 5kg Zn in 25kg slabs		
Sample 3	Copper scrap various from a few grams to 50kg Zn in 25kg slabs		

Table8-3: Leaded brass samples charge weight (http://www.lcl.com.au)

Sample Name	**Rod Dia. (mm)**	**Continuous Casting Types**
Sample 1	28	Horizontal
Sample 2	28	Horizontal
Sample 3	28	Horizontal

Table 8-4: Leaded brass samples target range (http://www.lcl.com.au)

Element	**Target Range**	**UNS Number**
Bi	0.6 - 0.7	Nearest Alloy Designation is C28XXX (pending application with Copper Development Association - CDA).
Sn	0.3	
Pb	0.1 – 0.2	
As	0.09 – 0.13	
Zn	36.6 – 37.5	

8.2.2 Metallography

Samples for metallographic examination were prepared by conventional techniques. Metallographic sections were cut with a clean sharp hacksaw and then ground using alumina grinding paper, first using coarse abrasive paper (grade no. 220) and subsequently wet & dry fine paper (grit no. 1200) by 5-10 lbs force and water as a lubricant. Base/head speed of grinding was 100/100 rpm.

The samples were then polished using diamond paste beginning with 1 micron and then subsequently using ¼ micron. Base/head speed of polishing was 100/100 rpm and the force was 5-10 lbs. Following by polishing respectively, rinsing in alcohol and drying in a hot air stream were used as finishing procedures.

According to the ASTM E407-07 (Standard Practice for Micro-Etching Metals and Alloys), the polished samples were etched in a solution of 70% concentrated nitric acid (HNO_3) and water. Samples structure was investigated using a Keyence VHX 3D digital microscope.

Metallographic samples were examined in brightfield reflected light modes and then images were taken with a Keyence VHX 3D digital microscope camera and then processed using Keyence VHX 3D digital microscope image software.

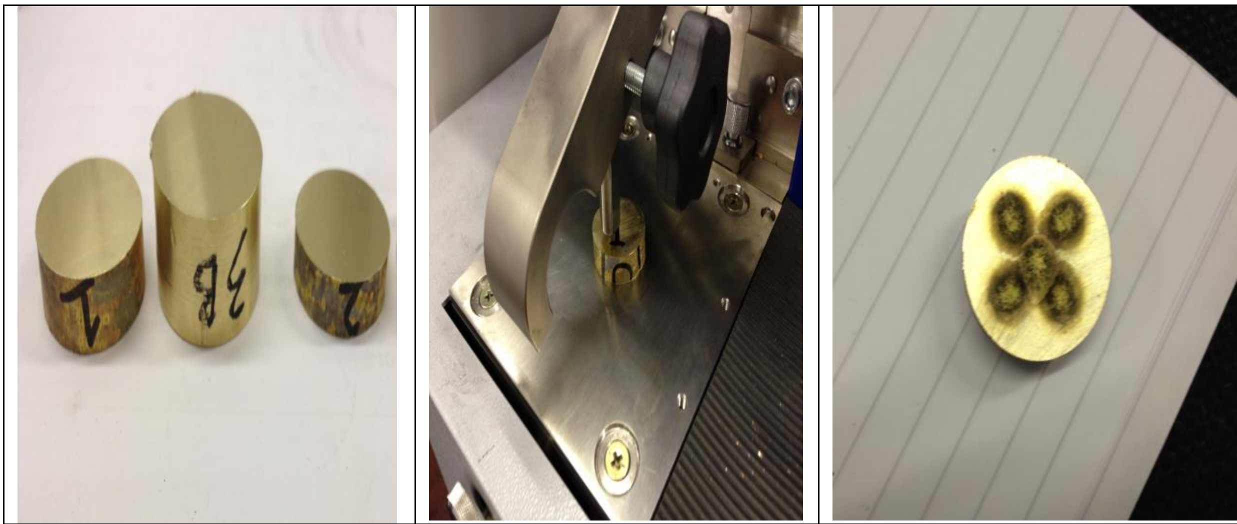
8.2.3 Mass Spectrometry Analysis

(1) Mass spectrometry (MS), (2) wet chemistry including gravimetric and titrimetric techniques, (3) spark optical emission spectroscopy (Spark-OES), (4) inductively coupled plasma-optical emission spectroscopy (ICP-OES), (5) X-ray fluorescence (XRF), and (6) X-ray diffraction (XRD) are common analytical chemistry techniques to identify the amount and type of chemicals present in a sample.

The mass spectrometer has a few advantages over the other analytical methods such as small sample size, accuracy, fast analysis and less demanding safety issues as compared to the X-ray techniques (Sparkman, 2000) , (R. García, 2012) , (Beckhoff, 2006) and (Semih Otles).

In this research mass spectrometry was used (model: AMETEK) as an analytical technique to identify the amount of chemicals present in samples.

The samples were prepared using a milling machine. Figure 8-4 shows photographic images of samples before, during and after mass spectrometry analysis.



(a) Samples before mass spectrometry analysis	(b) Samples during mass spectrometry analysis	(c) Samples after mass spectrometry analysis

Figure 8-4: Spectrometry analysis

8.2.4 SEM/EDX

A scanning electron microscope was employed to produce high resolution images. Energy dispersive X-ray spectroscopy analysis is a well-known X-ray technique used to identify the elemental composition of materials.

In this report a JEOL JSM7400F field emission scanning electron microscope were used at 20kV with shottky fieldemission gun scanning electron microscope equipped with secondary and backscattered electron detectors and an EDX energy-dispersive X-ray spectroscopy (EDS) system for elemental analysis. It’s done to confirmation a dark spot Pb particle.

8.3 Results and Discussion

The results is divided to three major sections. These sections are described the analysis data for metallography, SEM/EDX and mass spectrometry atest respectively.

8.3.1 Results and Discussion from Optical Microscope

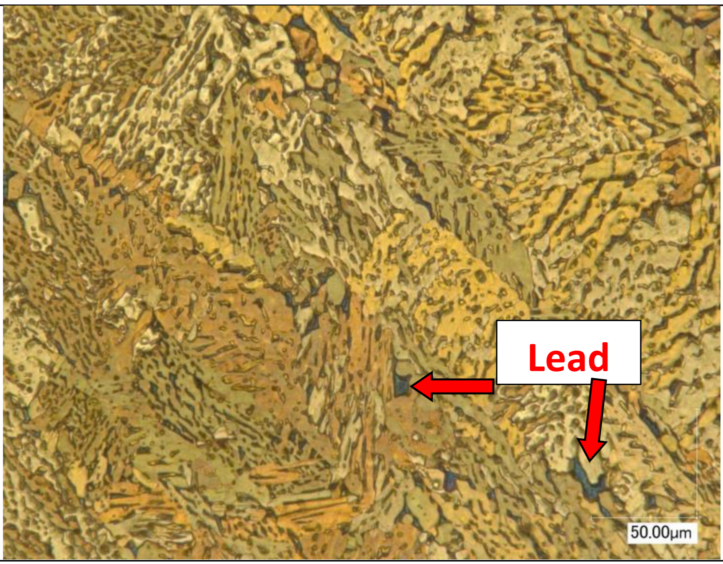
The grain structure of the leaded brasses is similar to the unleaded brasses (http://www.copper.org, n.d.).

The microstructure of the leaded brasses is containing lead particles mainly in the grain boundaries or inter-dendritic regions. Lead is practically insoluble in solid copper and is appear as a dark particle in the structure (García, 2010).

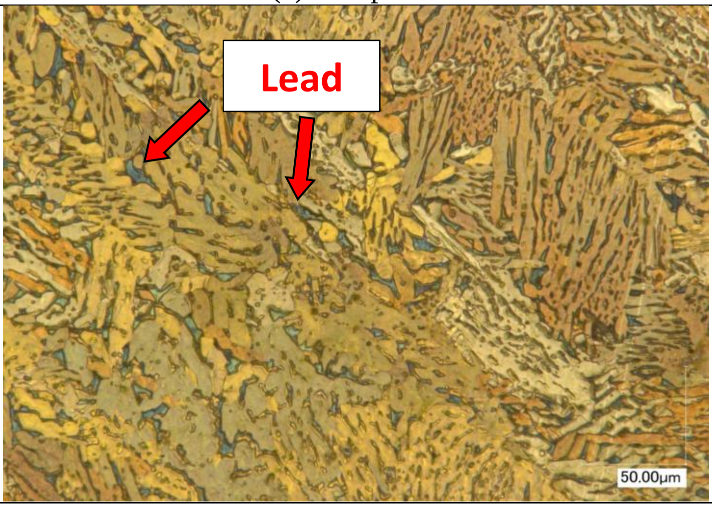
In order to identify lead, the samples were examined under digital optical microscope (magnification x1000).

Figure 8-5 shows the typical equiaxial grain morphology structure of brass samples and high insoluble Pb as a dark particle. The Pb content was too low to draw any important conclusion about the homogeneity of Pb in the samples. However it loosely appeared to be fairly well distributed.

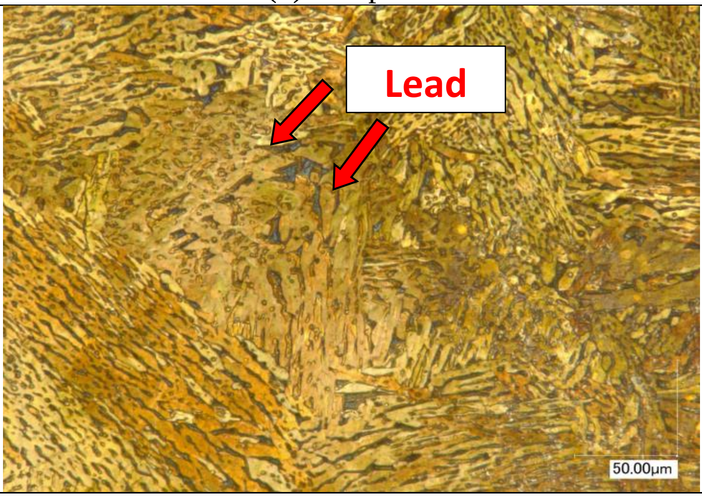
Lead is insoluble in brass at the solid state and forms “island” consisting of spherical particle occupying α and β interfaces. The decrease of mean particle diameter and the increase of particle population density (for given lead content) result in a substantial improvement in machinability.



(a) Sample. 1



(b) Sample. 2



(c) Sample. 3

Figure 8-5: Cross section of the microstructure of leaded-brass sample

8.3.2 Results and Discussion from Mass Spectrometry Analysis

The work was continued using the AMETEK spectrometer to examine different areas on each specimen. Areas 1 through 4 are around the circumference of the sample, and area 5 is in the middle. Results show that there is no significant difference in the distribution of any one of the elements based on the mass spectrometry result. Following Table 8-5 and Figure 8-6 present the findings.

Table8-5:The leaded-brass mass spectrometry results

Sample No: 1					
Location	**Zn**	**Pb**	**Sn**	**As**	**Bi**
1	35.956	0.187	0.338	0.142	0.690
2	36.036	0.188	0.333	0.140	0.685
3	36.530	0.187	0.331	0.139	0.681
4	36.456	0.187	0.328	0.138	0.681
5	36.476	0.183	0.330	0.136	0.678

Sample No: 2					
Location	**Zn**	**Pb**	**Sn**	**As**	**Bi**
1	37.073	0.200	0.314	0.115	0.714
2	36.836	0.199	0.314	0.115	0.713
3	36.866	0.198	0.314	0.114	0.714
4	37.163	0.199	0.313	0.115	0.715
5	37.120	0.196	0.312	0.113	0.704

Sample No: 3					
Location	**Zn**	**Pb**	**Sn**	**As**	**Bi**
1	36.316	0.140	0.279	0.101	0.669
2	36.580	0.124	0.277	0.100	0.677
3	36.690	0.123	0.276	0.099	0.675
4	36.643	0.123	0.277	0.099	0.673
5	36.316	0.124	0.278	0.100	0.676

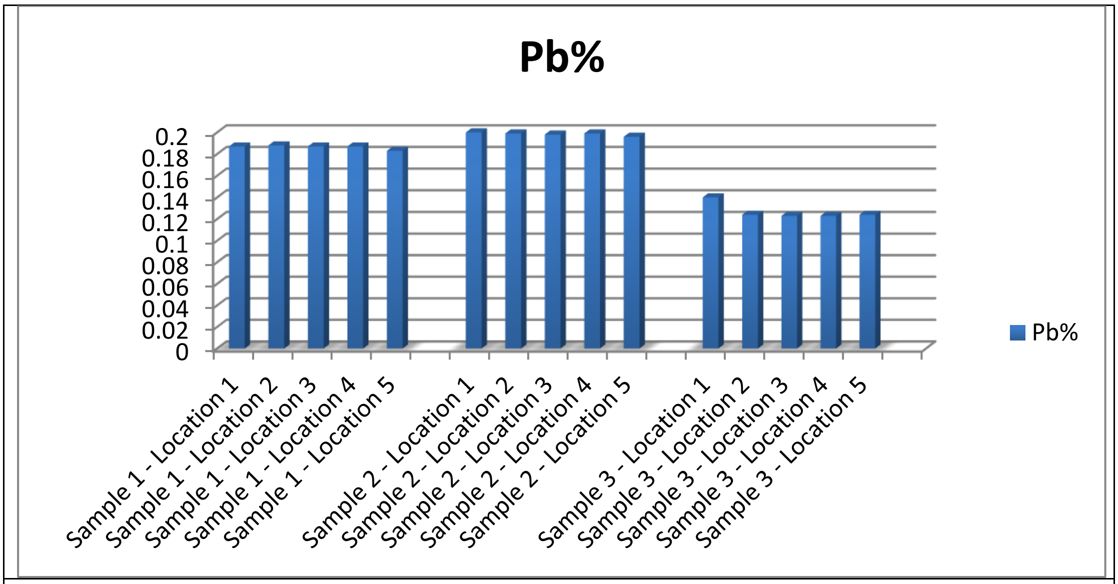


Figure 8-6: The leaded brass mass spectrometry results

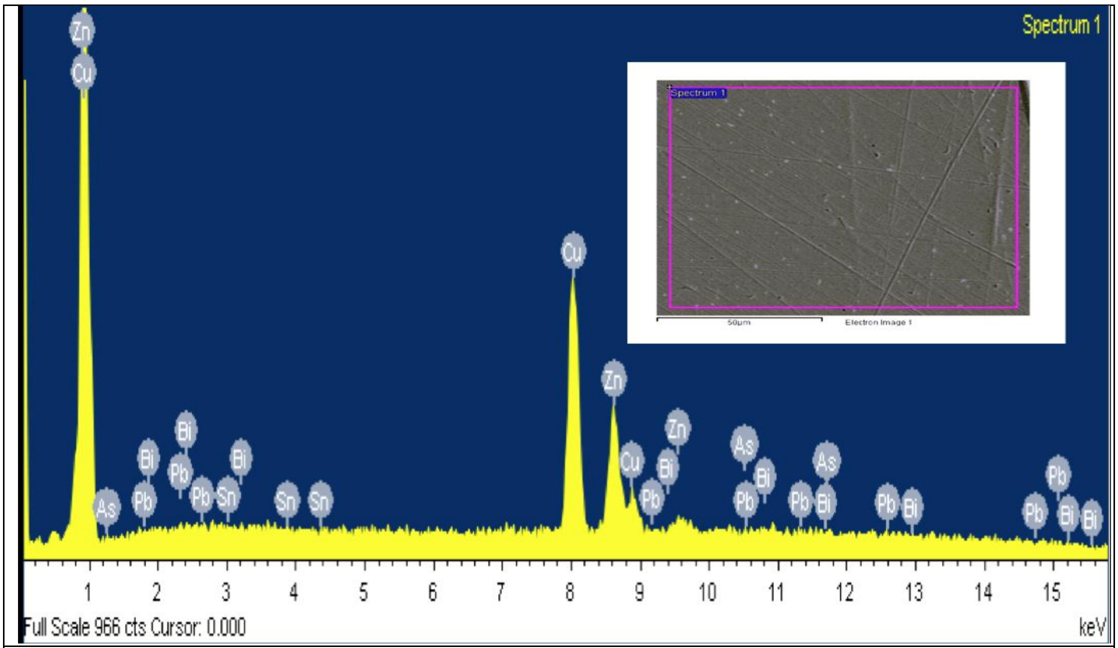
Analysis of variance was carried out on the samples to observe any difference between the groups on some variable using ANOVA.

ANOVA is a statistical procedure to analyse the difference between two or more means and is used to analyse general alternately specific difference between means (Jeff Miller, 2006).

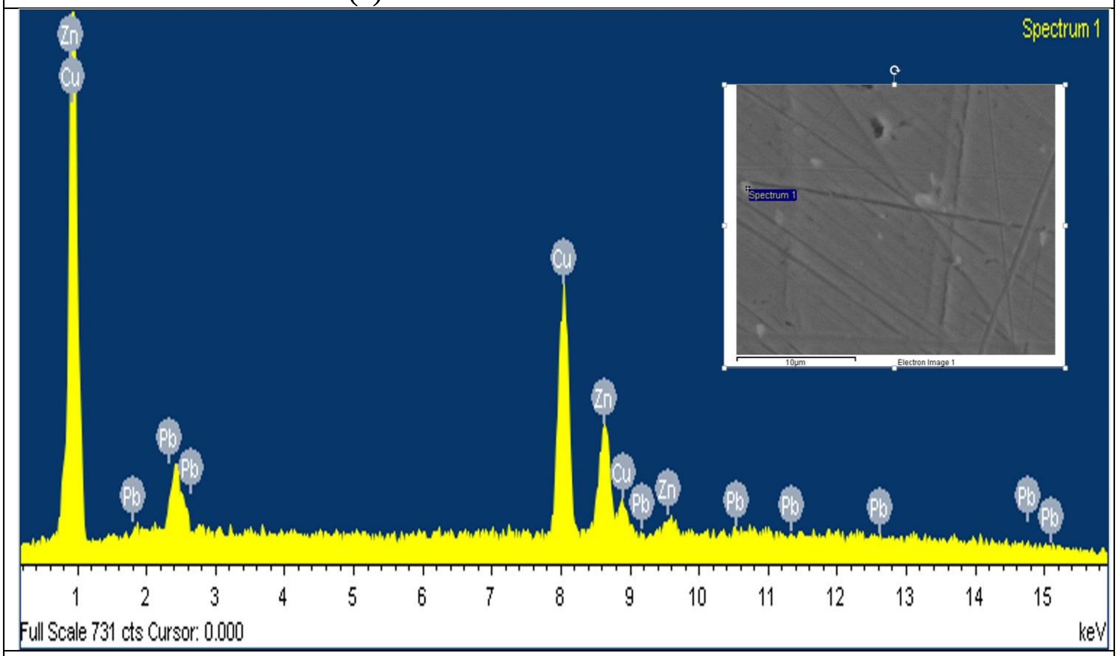
As we see in the above chart, we have three groups of samples, labelled 1, 2, 3. There is a target range for samples: the aim is that the sample should be located within this range, and then the statistical method of ANOVA is applied over these samples. From this analysis, the results fall perfectly in the target range, i.e. the ANOVA analysis of variance failed to reject the null hypothesis with a confidence level of $\alpha = 0.05$. This means that there is no proven significant difference in any of the samples tested on the spectrometer based on their respective areas of testing.

8.3.3 Results and Discussion from SEM Image Observation and EDX Analysis

Figure 8-7 shows the structure of brass samples. The peaks corresponding to the elements, which were generated by the EDX analysis, show the overall texture of the sample to be Cu and Zn. In addition, the bright particles have been determined using selected point area EDX analysis and Pb was identified as appear on optical microscope. The performed SEM/EDX analysis on the samples demonstrated that the distribution of elements inside each individual sample is homogeneous, which confirm the result from the optical microscope and mass spectrometry analysis.



(a) SEM and EDX of overall feature



(b) SEM and EDX of bright particle

Figure 8-7: SEM/EDX analysis of leaded brass samples

8.4 Conclusion

The obtained results regarding the investigation of the distribution of lead in 3 different combinations of brass feedstock by mass spectrometer, digital optical microscope and SEM/EDX can be summarised in the following points:

1- Following on from the mass spectrometry results, the distribution of elements inside each individual sample is homogeneous.

2- Homogenised distribution of lead in 3 different combinations of brass feedstock by mass spectrometer has been confirmed by ANOVA analysis.

3- Regarding to the Optical microscopy and SEM and EDX analysis done on the samples, the distribution of lead inside each individual sample is homogeneous.

4- Based on mass spectrometry could not find a great deal of variation within each samples based on sampling 5 different locations.

5- All analysis confirmed that the lead content can be fairly well distributed in brass based on using any kind of casting charge (copper scrap or brass scrap or casting granules). Obviously brass scrap is cheaper than either copper scrap or copper granules. So, either cheaper charge (brass scrap or copper scrap) has good potential to be adapted to the mass production of leaded brass produce by the continuous casting process.

8.5 Recommendation

As for future work, this research can be extended to investigate lead using X-ray fluorescence (XRF) machine, which is categorised as non-destructive analysis.

Chapter 9 - Conclusion and Future work

Conclusion:

The factors determining business success and successful internationalization are many and varied, such as market conditions, the nature of the product, advertising. But one major factor that appears in almost all successful businesses is “continuous innovation”.

Due to globalized markets and worldwide activities, companies today have to deal with more challenging market dynamics in a highly volatile production environment. Since companies from high-wage countries (such as UK) cannot compete with companies from low-wage countries (such as India or China) from a direct cost perspective, they must try to meet customer’s demands by offering highly individualized and customized products.

In the present thesis, in particular, significant progress has been made in establishing a range of process and product improvements supported by relevant characterisation techniques. A significant amount of data has been provided that has directly benefited a number of Research and Development (R&D) projects. Successful results from these R&D projects in turn have a significant impact on both current and, more significantly, future business growth. A number of suggestions for future directions have been given at the end of each experimental chapter.

R&D activities, with access to enhanced equipment and laboratory facilities, have significantly helped Rautomead to investigate the feasibility of processing a number of new alloys (such as CuZr), or provided the possibility of producing existing materials (such as Pb, PbSb and copper DHP tube), by a new manufacturing process which reduces operating costs, production time and/or capital cost requirements.

These research activities have been mainly focused on the material characterisation of copper alloy rod and tube produced by continuous casting and other fabrication processes. The characterization work for these materials has been important to evaluate and compare with the continuously cast copper alloy products, and additionally to improve the capacity and performance of Rautomead continuous casting equipment. To optimise the casting processes and improve the performance of the cast copper alloys, the following characterisation work has been carried out:

- Establishing an analysis technique to measure and display grain size of DHP copper tube.
- Establishing an analysis technique to perform expanding drift tests on DHP copper tube.
- Identifying the grain refinement techniques of copper alloy by thermal method (water flow rate, casting speed, pull distance, liquid metal temperature, cleanout cycle, continuous casting direction (horizontal /vertical) and super-cooler size).
- Extensive work on the grain refinement techniques of copper alloy by mechanical techniques (mechanical agitation such as mould vibration, stirring of the melt, rotation of the mould and rheocasting).
- Identifying the grain refinement techniques for various copper alloys by chemical method (nucleant agent addition into the melt) including: size of nanoparticles, preparation of nanoparticles, grain refining procedure and review of current problem statements.
- Establishing an analysis technique to display and measure the size, depth, width and shape of surface cracks in continuously cast rod.
- Effect of antimony addition relative to microstructure and mechanical properties of continuously cast lead alloy.

- Investigation of the distribution of lead in three different combinations of brass feedstock.

These investigations have helped Rautomead develop its technology and tooling for the manufacture and processing of both new alloys and materials, and also to produce known materials by using continuous casting as an innovative production process. Examples include:

1. Support in establishing casting parameters to continuously cast DHP copper tube (development of a new process for existing material).
2. Support in establishing casting parameters to continuously cast copper zirconium (CuZr) alloy for new automotive applications (development of a new process for a new alloy series).
3. Support in establishing casting parameters and process to continuously cast lead (Pb) and lead antimony (PbSb) (development of a new process for an existing material, currently produced by alternative process).
4. Support for a Rautomead customer in the development and registration of a new alloy category (brass).

The application of advanced microscopy and analysis techniques coupled with the development of in-house casting assessment expertise, facilities and methodologies are leading to a step-change in process validation capabilities, when applied to the increasing range of complex alloys which the company receives enquiries to design and provide equipment for.

Each of these examples have helped secure Rautomead’s position for future business success through the strengthening of the technical capability and product offering. They also help by extending the technical understanding and product and process knowledge through improved material characterisation and analysis techniques. These successes will be vital in securing the company's leading global position as a provider of specialised niche product casting equipment, enhancing job security and job creation in the UK based on its leadership in chosen markets. New application areas (such as CuZr) will support advanced manufacturing customer companies in implementing highly efficient continuous casting technologies in their production processes, thus reducing costs and improving competitive position.

As a summary. This PhD work helped Rautomead to improve profit and control in manufacturing business. As a particular example;

- CuZr trial; machine sold to Japan valued approximately €1 million,
- Brass and Aluminum Bronze trial; machine sold to Spain valued approximately €1.4 million
- CuAg trial; machine sold to Japan valued around €1 million.
- CuMg trial; machine sold to Turkey valued approximately €1 million.
- Lead trial; machine sold to US valued approximately $1 million.

Future work:

The future work in this PhD thesis will be:

- The development of casting capability of a range of copper alloys using new alloying elements such as Fe, Ti, Cr
- The development of casting capability for non-copper metals and alloys such as magnesium, zirconium alloy
- Continue development of casting capability to produce DHP copper tube
- Process optimisation
- Improve manufacturing yield

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Appendix: Conference, seminar, workshop and training course attendances related to this work:

Conference attendances related to this work:

- 25th International Conference on Metallurgy and Materials, (Brno, Czech Republic, 2016)
- ECCC 2014 – 8th European Continuous Casting Conference & Symposium Numerical and physical modelling (Graz, Austria - 2014).
- ICMMSE 2014 International Conference on Metallurgy and Material Science and Engineering (Venice, Italy - 2014)
- 23rd International Conference on Metallurgy and Materials, (Brno, Czech Republic, 2014).
- ICMMS 2014 International Conference on Metallurgy and Material Science (Zurich, Switzerland - 2014)
- The 2nd International Conference on Material Science and Engineering Technology, (London -2013)

Seminars attendances related to this work:

- Latest Developments on Refractory Coating Seminar, (Institute of Cast Metal Engineer - Stepps, Scotland- 2015)
- An Overview of the UK Foundry Industry Seminar, (The University of Buckingham and cast metal federation - Stepps, Scotland – 2013)
- Latest Development of Non Ferrous Melting Seminar, (Institute of Cast Metal Engineer - Motherwell, Scotland- 2013)

Workshop/Traning course attendances related to this work:

- Principles of Testing & Quality Assurance (University of Sheffield, England 2014)
- XRF Radiation Safety Training (OLYMPUS, Scotland- 2014)
- Working with Industry seminar about how Research and Innovation Services (RIS) and The Innovation Portal can help with industry engagement. (Dundee Technopole, Dundee University Incubator, 2014)
- Duelling 3D Printers workshop (The innovation portal, academic expertise for Scottish business, 2014)
- RS3000 Finite Element Analysis- Steady State Thermal Stress Analysis for Design, (AMEC Commercial, Scotland – 2013)
- Introduction to the Advanced Materials Research Laboratory, (University of Strathclyde, Glasgow-2013)
- Principle of continuous casting (Rautomead, Scotland- 2012)
- Principle of SEM Scanning Electron Microscope (University of Dundee – Advanced Materials Centre, Scotland- 2012